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(54) **Oxoindolizine and oxoindolizinium dyes and processes for their preparation.**

(57) Oxoindolizine and oxoindolizinium dyes are novel compounds useful in image formation such as in laser recording and reading. The dyes are formed by (1) the reaction of a cyclopropanone compound with a pyridine compound and optionally (2) by reaction of the product from (1) with a color-forming compound preferably in the presence of an oxidant.

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OXOINDOLIZINE AND OXOINDOLIZINIUM DYES AND
PROCESSES FOR THEIR PREPARATION

This invention relates to new oxoindolizine and oxoindolizinium dyes and to their preparation.

5 Dyes useful in imaging materials are well known in the photographic art. However, of the various types of dyes available or described in the prior art, no class is known which offers the combined advantages of wide absorption ranges and
10 ease of preparation without the need for complex multistep reactions.

Attempts have been made to react cyclopropenones with heteroaromatic nitrogen compounds as described in, for example, "Reaction of Cyclopropenones With Heterocyclic Nitrogen Compounds" by J.
15 W. Lown and K. Matsumoto, Canadian Journal of Chemistry, Vol. 49, 1971, pages 1165-1175. However, such attempts did not produce oxoindolizine or oxoindolizinium dyes. None of the known classes of
20 dyes involve preparation by means of a simple reaction of a cyclopropenone with a pyridine compound nor do they involve reactions of (1) color-forming couplers with (2) products derived from reaction of photosensitive cyclopropenones with
25 pyridine compounds. This invention provides dyes which are easily synthesized and which have a variety of uses in imaging technology.

The new oxoindolizine and oxoindolizinium dyes provided by this invention are useful in laser
30 recording and reading applications. Some of these dyes are also useful as image dyes in photothermography and thermography.

Oxoindolizine and oxoindolizinium dyes described herein include methyleneoxoindolizine,
35 (4-oxoarylene)oxoindolizine, bis-oxoindolizine, bis(oxoindoliziny1) ethylene, (2- and 4-amino-

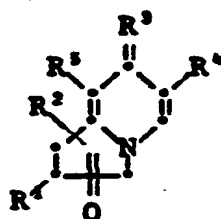
-2-

arylene)oxoindolizine and pyridiniumoxoindolizine dyes. These dyes may be in their keto or enol form, but are also provided in their various isomeric and tautomeric forms.

5 Oxoindolizine dyes according to this invention, in their keto form, have the following structure:

(I)

10



15

wherein

R¹ and R² are individually straight or branched chain alkyl containing 1 to 18, preferably 1 to 10 carbon atoms; substituted or unsubstituted aryl containing 6 to 20 carbon atoms; or polystyryl having appended indolizine or indolizinium groups, or combinations thereof;

20 R³ is a divalent group which, with the oxoindolizine nucleus, completes an organic chromophore;

R⁴ is hydrogen; alkyl containing 1 to 18 carbon atoms; cyano; acyl containing 2 to 20 carbon atoms; carboalkoxy containing 2 to 18 carbon atoms; aminocarbonyl containing 1 to 18 carbon atoms; acyloxy containing 2 to 18 carbon atoms; bromine or chlorine; and

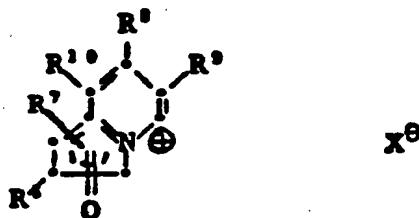
30 R⁵ is hydrogen; chlorine; bromine or alkyl containing 1 to 18 carbon atoms.

35

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Oxoindolizinium dyes according to this invention, in their keto form, have the following structure:

(II)



wherein

X^{θ} is an anion, preferably an acid anion;

R^6 and R^7 are individually straight or branched chain alkyl containing 1 to 18, preferably 1 to 10 carbon atoms; substituted or unsubstituted aryl containing 6 to 20 carbon atoms; or polystyryl having appended indolizine or indolizinium groups or combinations thereof;

R^8 is a monovalent group which, with the oxoindolizinium nucleus, completes an organic chromophore;

R^9 is hydrogen; alkyl containing 1 to 18 carbon atoms; cyano; acyl containing 2 to 20 carbon atoms; carboalkoxy containing 2 to 18 carbon atoms; aminocarbonyl containing 1 to 18 carbon atoms; acyloxy containing 2 to 18 carbon atoms, bromine or chlorine; and

R^{10} is hydrogen; chlorine, bromine or alkyl containing 1 to 18 carbon atoms,

Alkyl groups which are suitable for use as R^1 , R^2 , R^4 , R^5 , R^6 , R^7 , R^9 or R^{10}

substituents include, for example, methyl, ethyl and straight or branched chain propyl, butyl, amyl, decyl, dodecyl or lauryl.

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Aryl groups which are suitable for use as R^1 , R^2 , R^6 or R^7 substituents include, for example, unsubstituted or substituted phenyl tolyl, xylyl, methoxyphenyl, 4-t-butylphenyl, anisyl, naphthyl or methoxynaphthyl.

Examples of acyl groups which are suitable for use as R^4 and R^9 substituents include acetyl, propionyl, 2-ethylhexanoyl and stearoyl.

Examples of acyloxy groups which are suitable for use as R^4 and R^9 substituents include acetoxy, propionoxy, butyroxy and lauroxyloxy.

Examples of carboalkoxy and aminocarbonyl groups which are suitable for use as R^4 and R^9 substituents include, respectively, carbomethoxy, carboethoxy and carbobutoxy, and unsubstituted aminocarbonyl or methylaminocarbonyl, dimethylaminocarbonyl and ethylaminocarbonyl.

Examples of X anions are methanesulfonate, trifluoromethanesulfonate, paratoluenesulfonate, bromide, chloride, iodide and sulfinate.

The R^5 and R^{10} substituents, as defined above, are such that they have no adverse affect upon the desired dye properties of the described oxoindolizine and oxoindolizinium compounds.

Useful R^3 and R^8 groups are, for example

- a) substituted or unsubstituted heterocyclyl or heterocyclylidene groups optionally appended through methine and polymethine groups, such as 1) indolizine and indolizinium groups illustrated by structures (I) and (II) appended directly as the

-5-

respective R^1 and R^2 groups or appended through a substituted or unsubstituted methine or polymethine chain, such as containing 1 to 6 methine groups, ii) pyridylidene, iii) pyranyl, iv) pyranylidene, v) thiopyranyl, vi) thiopyranylidene, and vii) julolidyl; including the onium salts of such heterocyclyl and heterocyclylidene groups, such as the immonium, oxonium and sulfonium salts; and the acid addition salt derivatives of such heterocyclyl and heterocyclylidene groups;

b) substituted and unsubstituted aminoarylmethine and hydroxyarylmethine, including their tautomers, such as represented by the formula: (Z)(A)(D) wherein

Z is a methine or polymethine group, such as containing 1 to 6 methine groups;

A is a substituted or unsubstituted aromatic group, such as arylene containing 6 to 20 carbon atoms, for example, phenylene, phenylidene, naphthylene, and naphthylidene; and

D is $-OR^{120}$, $-NR^{120}R^{121}$, $=O$, or $-NR^{122}$ wherein R^{120} is a monovalent cation, preferably hydrogen, R^{120} and R^{121} are independently selected from hydrogen, substituted or unsubstituted alkyl, such as alkyl containing 1 to 20 carbon atoms, alkenyl, such as alkenyl containing 2 to 20 carbon atoms, and aryl, such as aryl containing 6 to 20

-6-

carbon atoms, including phenyl and tolyl; or, R^{130} and R^{131} taken together with (A) form a polycyclic heterocyclic group, such as a

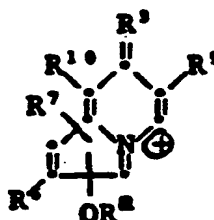
R^{132} is alkyl, such as alkyl containing 1 to 20 carbon atoms or aryl such as aryl containing 6 to 20 carbon atoms;

- c) a methylene group substituted with at least one, preferably two electronegative groups, such as acyl, cyano, aryl, alkoxycarbonyl, and aminocarbonyl groups; and
- d) a formyl group.

X^{\ominus} is an anion, for example, methanesulfonate, trifluoromethanesulfonate, para-toluenesulfonate, bromide, chloride, iodide, and sulfinate.

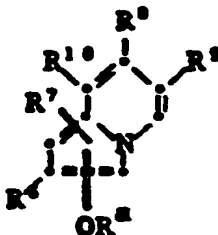
The term "enol" herein means an enol from the keto form of the dye as well as an enol produced by a protonation reaction or other reaction. For example, typical enols are represented by the formula:

(IIA)



or

(IIB)



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wherein X^{θ} , R^1 , R^2 , R^3 , R^4 , R^5 and R^{10} are as defined above and R^a is hydrogen or acyl.

5 The term "acyl" herein means alkylcarbonyl containing 2 to 20 carbon atoms and arylcarbonyl, such as arylcarbonyl containing 7 to 20 carbon atoms.

The term "aryl" means unsubstituted or substituted aryl containing 6 to 20 carbon atoms, such as phenyl, tolyl, xylyl, naphthyl, and
10 methoxyphenyl.

As noted above, the preparations of oxoindolizine and oxoindolizinium dyes of the invention do not involve complicated reaction steps as do the preparations of prior art dyes.

15 The oxoindolizine and oxoindolizinium dyes of this invention are prepared by

- 1) reaction of a cyclopropenone compound with a pyridine compound, or
- 20 2) reaction of a cyclopropenone compound with a pyridine compound and then with a color-forming compound, or
- 3) a condensation reaction. The term "condensation reaction" herein means a dehydration involving, for example, an
25 active methylene and a carbonyl group.

A useful pyridine compound does not contain a substituent in the 2- or 6-position on the pyridine ring. Pyridine compounds do not form oxoindolizine or oxoindolizinium dyes when
30 substituted in the 2- or 6-position, that is in the positions next to the ring nitrogen atom.

The oxoindolizine and oxoindolizinium dyes herein are alternatively named as indolizinone compounds.

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Many pyridine compounds are useful in forming a dye compound of this invention. Examples of useful pyridine compounds are represented by the formula:

(III)



wherein:

R¹¹ is hydrogen; alkyl containing 1 to 18 carbon atoms; cyano; acyl containing 2 to 20 carbon atoms; carboalkoxy containing 2 to 18 carbon atoms; aminocarbonyl containing 1 to 18 carbon atoms; acyloxy containing 2 to 18 carbon atoms; bromine or chlorine;

R¹² is hydrogen; alkyl containing 1 to 18 carbon atoms; cyano; acyl containing 2 to 20 carbon atoms; benzyl or pyridyl; and

R¹³ is hydrogen; chlorine; bromine or alkyl containing 1 to 18 carbon atoms.

Alkyl groups which are suitable for use as R¹¹, R¹² and R¹³ substituents include, for example, methyl, ethyl, decyl and dodecyl.

Acyl groups which are suitable for use as R¹¹ and R¹² substituents include acetyl, propionyl, 2-ethylhexanoyl, stearoyl and lauroyl.

Examples of carboalkoxy and aminocarbonyl groups which are useful as R¹¹ substituents include, respectively, carbomethoxy, carboethoxy and carbobutoxy, and unsubstituted aminocarbonyl or methylaminocarbonyl, dimethylaminocarbonyl and ethylaminocarbonyl.

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Acyloxy groups which are suitable for use as R¹¹ substituents include acetoxy, propionyloxy, butyryloxy and lauroyloxy.

5 Examples of useful pyridine compounds for preparation of dyes according to the invention are:

P-1 4,4'-Dipyridylethylene:



P-2 1-Methyl-4-(4-pyridyl)pyridinium-p-toluenesulfonate:



P-3 Pyridine:



25 P-4 4-Picoline:

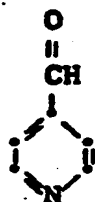


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P-5 4-Formylpyridine (also known as 4-pyridine-carboxaldehyde):

5



10

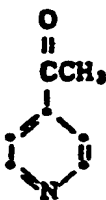
P-6 4-(4-Azastyryl)-1-methylpyridinium
p-toluene sulfonate:

15



P-7 4-Acetylpyridine:

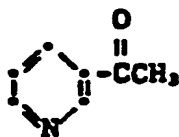
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P-8 3-Acetylpyridine:

30

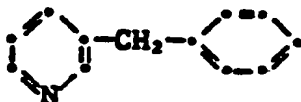


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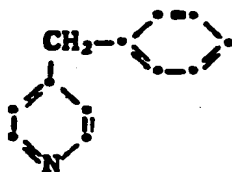
P-9 3-Benzylpyridine:

5



P-10 4-Benzylpyridine:

10



15

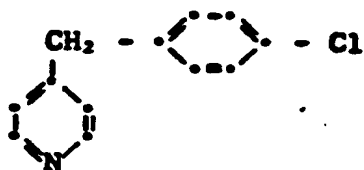
P-11 3-Bromopyridine:



20

P-12 4-(p-chlorobenzyl)pyridine:

25



P-13 3-Chloropyridine:

30



35

P-14 3-Cyanopyridine:

5



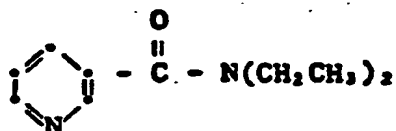
P-15 3,5-Dichloropyridine:

10



P-16 N,N-diethylnicotinamide:

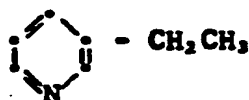
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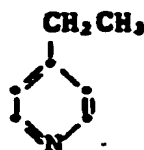
P-17 3-Ethylpyridine:

25



P-18 4-Ethylpyridine:

30

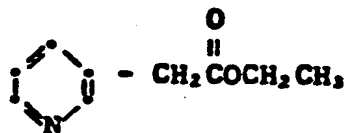


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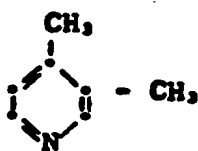
P-19 Ethyl-3-pyridylacetate:

5



P-20 3,4-Lutidine:

10



15

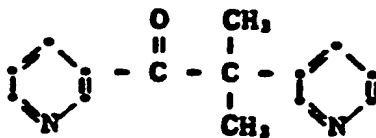
P-21 3,5-Lutidine:



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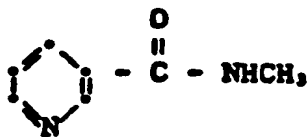
P-22 2-Methyl-1,2-di-3-pyridyl-1-oxo-propane:

25



P-23 N-methylnicotinamide:

30

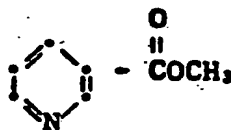


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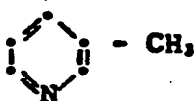
P-24 Methyl nicotinate:

5



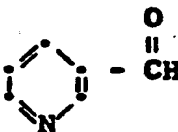
P-25 3-Picoline:

10



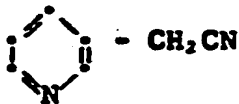
15 P-26 3-Formylpyridine (also known as 3-Pyridinecarboxaldehyde):

20



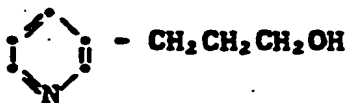
P-27 3-Cyanomethylpyridine (also known as 3-Pyridylacetonitrile):

25



P-28 3-(3-pyridyl)-1-propanol:

30



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P-29 Trans-1-(3-pyridyl)-2-(4-pyridyl)ethylene:



P-30 4-Cyanopyridine:

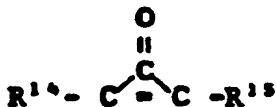


15 P-31 1-Benzyl-4-(4-pyridyl)pyridinium bromide:



20 Many cyclopropenone compounds are useful
for preparing dyes according to the invention.
Examples of useful cyclopropenones are represented
by the formula:

25 (IV)



30

35

wherein:

5 R^{14} and R^{15} are individually aryl containing 6 to 20 carbon atoms; aralkenyl containing 6 to 20 carbon atoms; alkyl containing 1 to 18, preferably 1 to 10 carbon atoms; or R^{14} and R^{15} together represent the carbon atoms necessary to complete a 7- or 8-member cyclic structure.

10 Aryl groups which are suitable for use as R^{14} and R^{15} substituents include, for example, unsubstituted and substituted phenyl, naphthyl or anthryl, such as methoxyphenyl and methoxynaphthyl.

15 Aralkenyl groups which are suitable for use as R^{14} and R^{15} substituents include for example, 2,2-diphenylvinyl, 2-phenylvinyl, 2-naphthylvinyl and 2-methyl-(2-phenylvinyl).

 Alkyl groups which are suitable for use as R^{14} and R^{15} substituents include methyl, ethyl, propyl, decyl and lauryl.

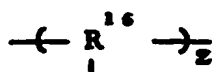
20 An example of an R^{14} and R^{15} cyclic structure is 2,3-pentamethylene.

 The aryl group of R^{14} and R^{15} is unsubstituted or substituted by one or more groups such as:

- 25 1) alkyl or alkoxy containing 1 to 5 carbon atoms, for example, methyl, ethyl, propyl, isopropyl, butyl, methoxy, ethoxy, propoxy and butoxy;
- 2) nitro;
- 30 3) aryloxy containing 6 to 10 carbon atoms, such as phenoxy and naphthoxy;

-17-

- 4) halogen, for example, chlorine, fluorine, iodine and bromine;
 5) a homopolymer or copolymer to which the aryl group is attached as a pendant moiety with the polymer having at least one repeating unit represented by the formula:



wherein:

R^{16} is a lower alkylene group containing from 1 to 5 carbon atoms; and

z is at least a portion of the number of repeating units in a polymer chain, such as 10 to 1000.

Examples of useful cyclopropenone compounds, some of which are described in U.S.

Patent No. 4,128,422, are:

2,3-diphenylcyclopropenone

2-(2-methoxynaphthyl)-3-phenylcyclopropenone

2-(2-methoxynaphthyl)-3-(4-methoxyphenyl)-cyclopropenone

2,3-bis(2-methoxynaphthyl)cyclopropenone

2,3-bis(2,4-dimethylphenyl)cyclopropenone

2,3-bis(4-n-butoxyphenyl)cyclopropenone

2,3-bis(4-methoxyphenyl)cyclopropenone

poly[styrene-co-4-(2-phenylcyclopropenonyl)-styrene]

2,3-bis(4-phenoxyphenyl)cyclopropenone

2-(4-n-butoxyphenyl)-3-phenylcyclopropenone

2-(2,5-dimethylphenyl)-3-phenylcyclopropenone

2-(4-methoxyphenyl)-3-phenylcyclopropenone

2-(2,4-dimethoxyphenyl)-3-phenylcyclopropenone

- 2,3-bis(2,4-dimethoxyphenyl)cyclopropenone
2,3-bis(2-methyl-5-isopropylphenyl)cyclo-
propenone
2,3-bis(3-nitrophenyl)cyclopropenone
5 2,3-bis(2,5-dimethylphenyl)cyclopropenone
2,3-bis(4-methylphenyl)cyclopropenone
2,3-di-n-propylcyclopropenone
2,3-pentamethylenecyclopropenone
2-(2,4-dimethoxyphenyl)-3-(2,4-dimethyl-
10 phenyl)-cyclopropenone
2,3-bis(2,5-dimethoxyphenyl)cyclopropenone
2-(2,4,6-trimethylphenyl)-3-phenylcyclo-
propenone
2-phenyl-3-(2,5-dimethoxyphenyl)cyclopro-
15 penone
2-phenyl-3-(2,4-dimethylphenyl)cyclopro-
penone
2,3-bis(2,2-diphenylvinyl)cyclopropenone
2,3-bis(2-methyl-2-phenylvinyl)cyclopropenone

20 The described cyclopropenones are prepared
by processes known in the organic synthesis art.

The cyclopropenone compounds may be
spectrally sensitized using procedures and
compounds known in the photographic art, such as
25 described in U.S. Patent No. 4,128,422.

The color-forming compound may, for example,
be a photographic color-forming coupler as used in
silver halide color photography.

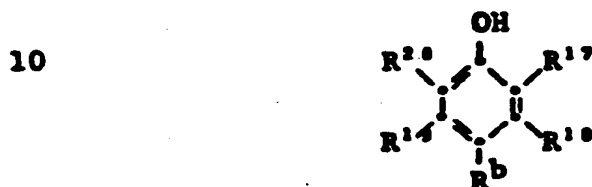
Especially useful phenolic, aniline and
30 active methylene couplers for forming dyes
according to this invention are those which are
known to be useful in the photographic art for
producing dye images.

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The term "phenolic coupler" herein means a phenolic or naphtholic compound which forms a dye by reaction with a described oxoindolizine or oxoindolizinium compound.

5 Examples of useful phenolic couplers are represented by the formula:

(V)



15 wherein:

R^b , R^{17} , R^{18} , R^{19} and R^{20} individually represent substituents which do not adversely affect the desired indolizine and indolizinium dyes, such as by altering the solubility or desired dye hue, and individually represent substituents that are useful in phenolic couplers in the photographic art, such as described in, for example, U.S. Patent No. 3,620,747, the description of which is incorporated herein by reference. In Structure V at least one of R^{17} ,

25 R^{18} and R^b is hydrogen. For example,

R^b , R^{17} and R^{18} are individually hydrogen; hydroxyl; alkyl containing 1 to 22 carbon atoms, such as methyl, ethyl, propyl and decyl; aryl containing 6 to 20 carbon atoms, such as phenyl and tolyl; amino; carboxamido; sulfonamido; sulfamyl; carbamyl; halogen; such as chlorine, fluorine, bromine and iodine; and alkoxy containing 1 to 18 carbon atoms, such as methoxy, ethoxy and propoxy;

35

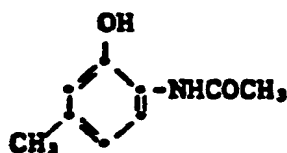
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$R^{1'}$ and $R^{2'}$ are individually hydrogen, alkyl containing 1 to 22 carbon atoms, such as methyl, ethyl, propyl and decyl; aryl containing 6 to 20 carbon atoms, such as phenyl and tolyl; amino; carboxamido; sulfonamido, sulfamyl; carbamyl; halogen, such as chlorine, fluorine, bromine and iodine; and alkoxy containing 1 to 18 carbon atoms, such as methoxy, ethoxy and propoxy; or $R^{1'}$ and $R^{2'}$ taken together represent the atoms necessary to complete a benzo group which is unsubstituted or substituted by at least one of the groups given for $R^{1'}$;

Examples of useful phenolic couplers are:

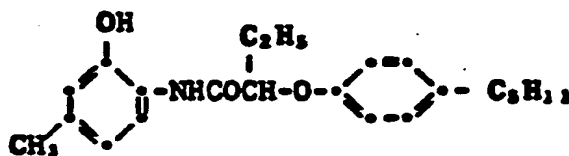
20 C-1

2-Acetylamino-5-methylphenol



25

C-2

2-[α -(4'-tert.-amylphenoxy)-butyrylamino]-5-methyl-1-phenol

30

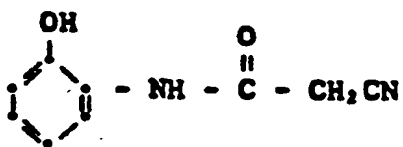
35

-21-

C-3

2-cyanoacetamidophenol

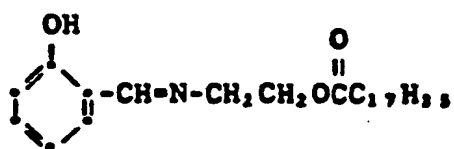
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C-4

2-(2-stearoyloxyethyl)iminomethylphenol

10

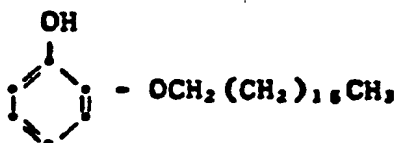


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C-5

2-octadecyloxyphenol

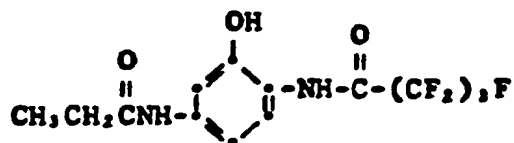
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C-6

2-perfluorobutyramido-5-propionamidophenol

25

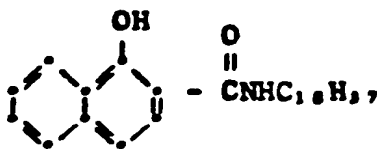


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C-7

2-octadecyl aminocarbonyl-1-naphthol

35

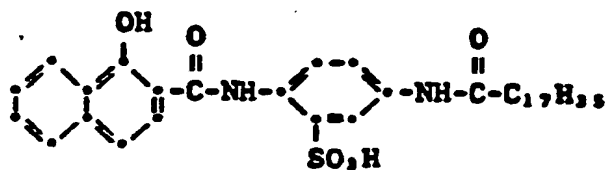


-22-

C-8

2-(2-sulfonyl-4-stearoylamino
anilinocarbonyl)-1-naphthol

5

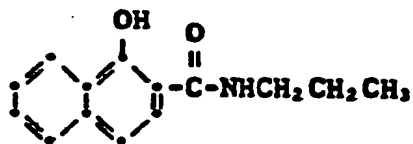


10

C-9

2-(propylaminocarbonyl)-1-naphthol

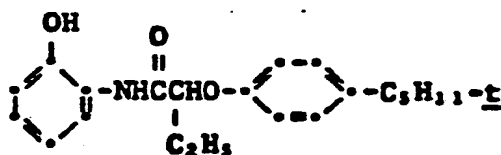
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C-10

2-[α-(4-tert-amylphenoxy)butyryl
amino]phenol

20

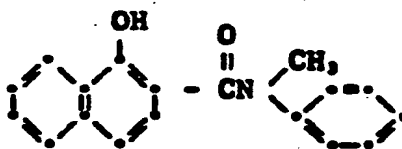


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C-11

2-(N-methylanilinocarbonyl)-1-
naphthol

30



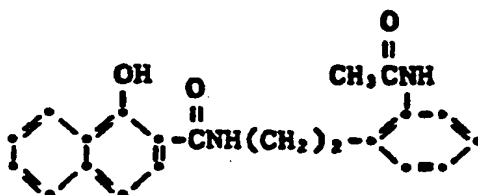
35

-23-

C-12

2-[2-(2-acetamidophenyl)ethyl
aminocarbonyl]-1-naphthol

5

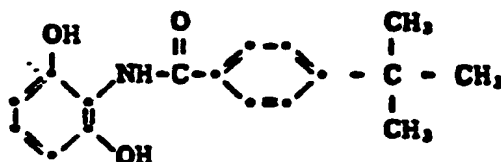


10

C-13

2-(4-tert-butylbenzamido
resorcinol

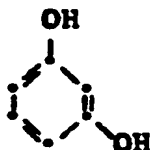
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C-14

resorcinol

20

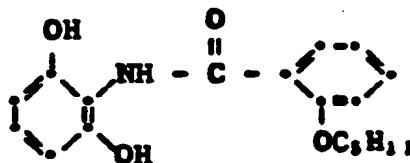


25

C-15

2-(2-amyloxybenzamido)resorcinol

30



35

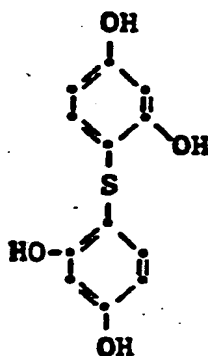
-24-

C-16

bis-4,4'-resorcinyll sulfide

5

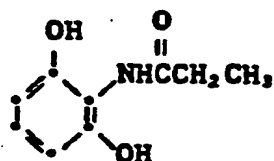
10



C-17

2-propinoamidoresorcinol

15

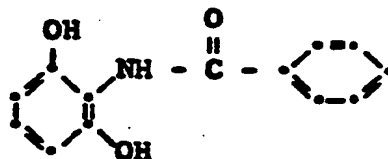


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C-18

2-benzamidoresorcinol

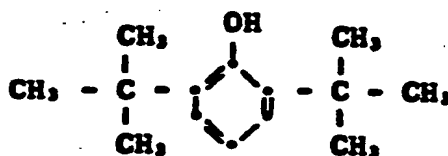
25



C-19

2,6-di-tert-butylphenol

30



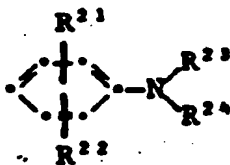
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-25-

The term "aniline coupler" herein means an aniline compound or related derivative which forms a dye by reaction with a described oxoindolizine or oxoindolizinium compound.

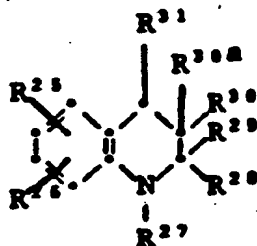
- 5 Examples of useful aniline couplers and derivatives thereof useful in forming oxoindolizine and oxoindolizinium dyes according to the invention are represented by the formulas:

10 (VI)



15

(VII)

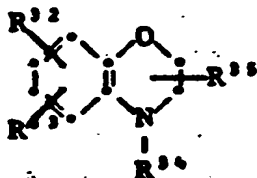


20

and

25

(VIII)



30

35

wherein

5 R^{21} , R^{22} , R^{23} , R^{26} , R^{32} and
 R^{33} are individually hydrogen; fluorine;
 chlorine; bromine; alkyl containing 1 to 6
 carbon atoms; cycloalkyl containing 3 to 10
 carbon atoms; alkoxy containing 1 to 4
 carbon atoms; phenoxy; alkylthio, such as
 alkylthio containing 1 to 4 carbon atoms;
 arylthio, such as arylthio containing 6 to
 10 20 carbon atoms; and groups represented by
 the formula $-NH-X-R^{36}$ in which X is $-CO-$,
 $-COO$ or $-SO_2-$;

15 R^{23} , R^{24} , R^{27} and R^{34} are
 individually selected from hydrogen;
 cycloalkyl, such as cycloalkyl containing 6
 to 20 carbon atoms; straight or branched
 alkenyl containing 2 to 10 carbon atoms;
 alkyl containing 1 to 18 carbon atoms, or
 20 R^{23} and R^{24} together represent the
 atoms necessary to complete a 5- or
 6-member heterocyclic ring with the
 nitrogen atom to which they are bonded,
 such as atoms completing a pentamethylene,
 ethyleneoxyethylene or ethylenesulfonyl-
 25 ethylene group which forms a ring or a
 julolidyl group; or

R^{23} and R^{24} individually can be
 $-S-R^{37}$; wherein

30 R^{37} is alkyl containing 1 to 6 carbon
 atoms, phenyl, phenyl substituted with
 halogen, alkoxy containing 1 to 6 carbon
 atoms, alkanoylamino containing 1 to 6 carbon
 atoms, cyano or lower alkoxycarbonyl,
 pyridyl, pyrimidinyl, benzoxazolyl,
 35 benzimidazolyl, benzothiazolyl, triazolyl;
 SO_2R^{38} ; $-COOR^{38}$; $-OXR^{38}$;
 $-NH-X-R^{32}$; $-X-R^{32}$; $-OCO-R^{34}$;

-27-

-CONR³⁵R³⁶; -SO₂NHR³⁷;-SO₂NR³⁸R³⁹;R²⁸, R²⁹, R³⁰, R^{30a}, R³¹ and

R³³ are individually selected from hydrogen
 5 and alkyl containing 1 to 6 carbon atoms;

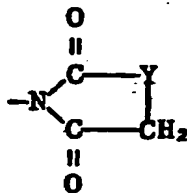
R³⁶ is alkyl containing 1 to 6 carbon
 atoms or alkyl substituted by a group that
 does not adversely affect the desired
 indolizine or indolizinium dye, such as
 10 halogen, hydroxy, phenoxy, aryl, such as aryl
 containing 6 to 20 carbon atoms, cyano,
 cycloalkyl, such as cycloalkyl containing 6
 to 12 carbon atoms, alkylsulfonyl containing
 1 to 6 carbon atoms, alkylthio containing 1
 15 to 6 carbon atoms, alkanoyloxy containing 1
 to 6 carbon atoms and alkoxy containing 1 to
 6 carbon atoms; when X is -CO-, then R³⁶ is
 also selected from hydrogen, amino, alkenyl
 containing 2 to 6 carbon atoms, alkylamino
 20 containing 1 to 6 carbon atoms,
 alkylcarbamoyl containing 1 to 6 carbon
 atoms, dialkylamino containing 2 to 12 carbon
 atoms, arylamino containing 6 to 12 carbon
 atoms, aryl containing 6 to 20 carbon atoms
 25 and furyl.

When R²³, R²⁴, R²⁷ or R³⁴ are alkyl,

the alkyl is unsubstituted or substituted by, for
 example, hydroxy, halogen, cyano, alkoxy containing 1
 to 6 carbon atoms, alkoxyalkoxy containing 2 to 8
 30 carbon atoms, hydroxyalkoxy containing 1 to 4 carbon
 atoms, succinimido, glutarimido, phenylcarbamoyloxy,
 phthalimido, phthalimidino, 2-pyrrolidono, cyclohexyl,
 phenoxy, phenyl or phenyl substituted by alkyl
 containing 1 to 6 carbon atoms, alkoxy containing 1 to
 35 6 carbon atoms, halogen, alkanoylamino containing 1 to
 6 carbon atoms, alkoxycarbonyl containing 2
 to 6 carbon atoms; sulfamoyl; alkylsulfamoyl

-28-

containing 1 to 6 carbon atoms; vinylsulfonyl;
 acrylamido; alkylsulfonamido, such as alkylsulfonamido
 containing 1 to 6 carbon atoms; phenylsulfonamido;
 alkoxycarbonylamino containing 1 to 6 carbon atoms;
 5 alkylcarbamoyloxy containing 1 to 6 carbon atoms;
 alkoxycarbonyloxy containing 1 to 6 carbon atoms;
 alkenylcarbonylamino containing 3 to 6 carbon atoms;
 groups represented by the formula:



wherein

20 Y is -NH-, -N-alkyl containing 1 to 6 carbon
 atoms, -O-, -S-, or -CH₂O-;
 R³³, R⁴⁰, R⁴¹, R⁴², R⁴³ and R⁴⁴
 are individually selected from unsubstituted
 alkyl containing 1 to 6 carbon atoms and
 25 alkyl containing 1 to 6 carbon atoms
 substituted by at least one group that does
 not adversely affect the desired
 oxoindolizine or oxoindolizinium dye, such as
 halogen, hydroxy, phenoxy, aryl containing 6
 30 to 20 carbon atoms, cyano, cycloalkyl
 containing 6 to 12 carbon atoms,
 alkylsulfonyl containing 1 to 6 carbon atoms,

35

-29-

alkylthio containing 1 to 6 carbon atoms,
alkanoyloxy containing 1 to 6 carbon atoms;
and alkoxy containing 1 to 6 carbon atoms,
and when X is -CO-, then R¹, R² and
5 R³ are also individually selected from
hydrogen, amino, alkenyl containing 2 to 6
carbon atoms, alkylamino containing 1 to 6
carbon atoms, alkyl carbamoyl containing 2 to
6 carbon atoms, dialkylamino containing 2 to
10 6 carbon atoms, arylamino containing 6 to 20
carbon atoms, aryl containing 6 to 20 carbon
atoms or furyl;

R⁴, R⁵, R⁶, R⁷ and R⁸ are
individually selected from hydrogen,
15 unsubstituted alkyl containing 1 to 6 carbon
atoms and alkyl containing 1 to 6 carbon
atoms substituted by at least one group that
does not adversely affect the desired
oxoindolizine or oxoindolizinium dye, such as
20 halogen, hydroxy, phenoxy, aryl containing 6
to 20 carbon atoms, cyano, cycloalkyl
containing 6 to 12 carbon atoms,
alkylsulfonyl containing 1 to 6 carbon atoms,
alkylthio containing 1 to 6 carbon atoms,
25 alkanoyloxy containing 1 to 6 carbon atoms
and alkoxy containing 1 to 6 carbon atoms,
cyano, alkanoyloxy containing 1 to 6 carbon
atoms, phenoxy, phenoxy substituted by at
least one of alkyl containing 1 to 6 carbon
30 atoms, alkoxy containing 1 to 6 carbon atoms,
and halogen.

The term "cycloalkyl" herein means an
unsubstituted cycloalkyl group or a cycloalkyl group
containing substituents that do not adversely affect
35 an oxoindolizine or oxoindolizinium dye according to
the invention. The cycloalkyl group, for example,

-30-

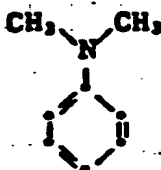
contains 3 to 7 carbon atoms and is unsubstituted or substituted by one or two groups selected from alkyl containing 1 to 4 carbon atoms, hydroxyl, alkoxy containing 1 to 4 carbon atoms, phenyl or phenyl
5 containing an alkyl group containing 1 to 4 carbon atoms, alkoxy containing 1 to 4 carbon atoms, halogen, alkanoylamino, cyano and alkoxycarbonyl, such as alkoxycarbonyl containing 1 to 4 carbon atoms.

10 Examples of useful aniline couplers are as follows:

AN-1

N,N-dimethylaniline

15

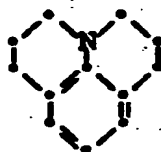


20

AN-2

julolidine

25



AN-3

N,N-diethylaniline

30

CH₃CH₂-N-CH₂CH₃

35

-31-

AN-4

N-phenylpiperidine



Examples of useful active methylene couplers for forming dyes according to the invention are represented by the formula:

(IX)



20 wherein:

Y^1 and Y^2 are the same or different electronegative groups, such as aryl containing 6 to 20 carbon atoms, such as phenyl and naphthyl; cyano; acyl containing 2 to 18 carbon atoms, such as acetyl, propionyl and butyryl; carboalkoxy containing 1 to 18 carbon atoms, such as carbomethoxy, carboethoxy, carbobutoxy and carboamyloxy; aminocarbonyl containing 1 to 18 carbon atoms, such as unsubstituted aminocarbonyl, methylaminocarbonyl, dimethylaminocarbonyl and ethylaminocarbonyl; or oxo-, thio- or selenopyrylium; or oxoindolizinium; or Y^2 is hydrogen; and

Y^3 is hydrogen or halogen, such as chlorine, bromine and iodine.

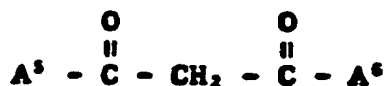
-32-

Preferred active methylene couplers are ketomethylene couplers. Other useful active methylene couplers include those known to be useful in the photographic art, such as pyrazalinone and coumarin couplers.

Examples of preferred ketomethylene couplers are represented by the formula:

(X)

10



wherein:

15

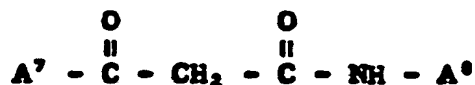
A^5 and A^6 are individually alkyl containing 1 to 18 carbon atoms, such as methyl, ethyl, propyl and amyl; aryl containing 6 to 14 carbon atoms, such as phenyl, naphthyl and anthryl; hydroxy; alkoxy, such as alkoxy containing 1 to 6 carbon atoms; amino; substituted amino; or thiol.

20

Ketocarboxamides are examples of especially useful ketomethylene couplers for forming dyes according to the invention. Examples of useful ketocarboxamides are represented by the formula:

25

(XI)



30 wherein:

35

A^7 and A^8 are individually alkyl containing 1 to 18 carbon atoms, such as methyl, ethyl, propyl, butyl, amyl, decyl and stearyl; and aryl containing 6 to 14 carbon atoms, such as phenyl, naphthyl, and anthryl; carbonyl; amino or vinyl.

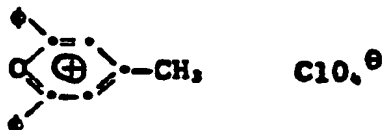
-33-

Other particularly useful active methylene couplers are alkyl flavylium salts and alkyl pyrylium salts, such as described in U.S. Patents 3,141,770 and 3,250,615.

5 Examples of useful methylene couplers include the following:

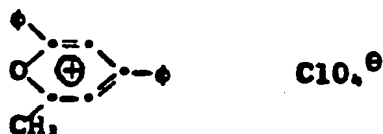
M-1 2,6-Diphenyl-4-methylpyrylium perchlorate

10



15

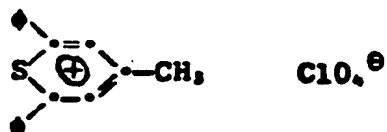
M-2 2,4-Diphenyl-6-methylpyrylium perchlorate



20

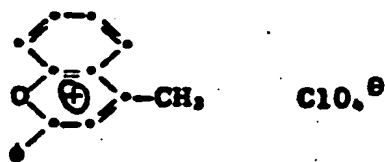
M-3 2,6-Diphenyl-4-methylthiopyrylium perchlorate

25



30

M-4 4-Methyl-2-phenylflavylium perchlorate

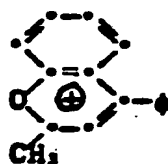


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-34-

M-5 2-Methyl-4-phenylflavylum perchlorate

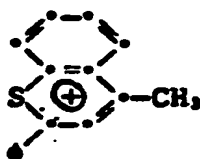
5

 ClO_4^-

10

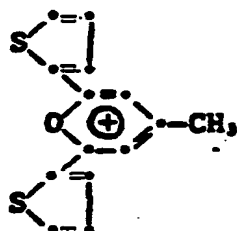
M-6 4-Methyl-2-phenylthioflavylum perchlorate

15

 ClO_4^-

M-7 2,6-di-(2-thiophenyl)-4-methylpyrylium
fluoborate

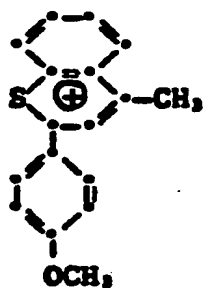
20

 BF_4^-

25

M-8 2-(4-methoxyphenyl)-4-methylthioflavylum
perchlorate

30

 ClO_4^-

35

-35-

M-9

2,4-pentanedione

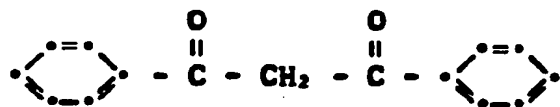
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M-10

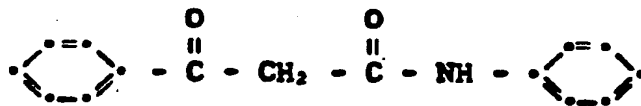
dibenzoylmethane

10



15 M-11

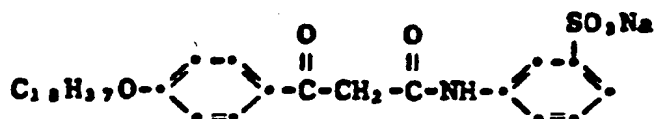
1-anilino-3-phenyl-1,3-propanedione



20

M-12

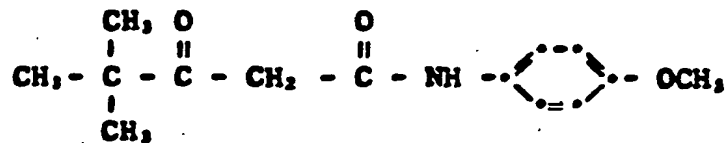
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M-13

1-tert-butyl-3-(4-methoxy anilino)-1,3-propanedione

30



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-36-

M-14

malononitrile

5



M-15

phenylacetonitrile

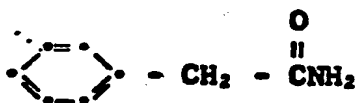
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M-16

phenylacetamide

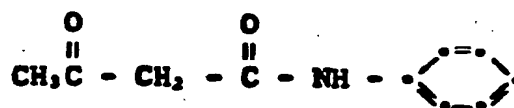
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M-17

N-phenyl acetylacetamide

20



25 M-18

bis-nitrophenylmethane



M-19

methyl cyanoacetate

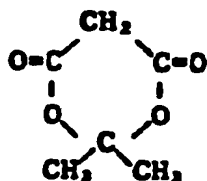
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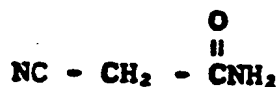
M-20

2,2-dimethyl-m-dioxane-4,6-dione



M-21

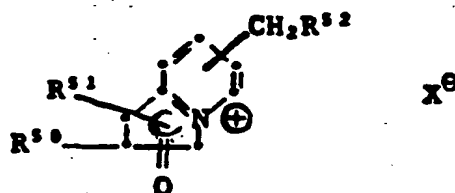
cyanoacetanide



The designation ϕ herein means a phenyl group.

Other particularly useful active methylene couplers are alkyl indolizininium salts represented by the formula:

(XII)



wherein

R^{s0} and R^{s1} are individually aryl containing 6 to 14 carbon atoms, such as phenyl, naphthyl, anthryl, methoxyphenyl and methoxynaphthyl; aralkenyl containing 6 to 14 carbon atoms, such as 2,2-diphenylvinyl, 2-phenylvinyl, 2-naphthylvinyl and 2-methyl(2-phenyl-

-38-

vinyl); alkyl containing 1 to 20 carbon atoms, such as methyl, ethyl, propyl, decyl and lauryl; or $R^{s'}$ and $R^{s'}$ together represent the carbon atoms necessary to complete a 7- or 8-member cyclic structure; and

$R^{s'}$ is a substituent which does not interfere with the coupling action of the indolizinium salt and does not adversely affect the desired properties of a resulting oxoindolizinium or oxoindolizine dye, such as hydrogen; carboxyl; alkyl containing 1 to 18 carbon atoms, for example, methyl, ethyl, propyl and dodecyl; cyano; and, aryl containing 6 to 20 carbon atoms, such as phenyl and xylyl;

X^{\ominus} is an anion as defined above, such as $CF_3SO_3^{\ominus}$, Br^{\ominus} and BF_4^{\ominus} .

Another method of preparation of oxoindolizine and oxoindolizinium dyes within Structures I and II comprises condensation of suitable indolizinols, indolizinones or indolizinium ions with active $-CH=$ compounds which complete an organic chromophore. Such indolizinols (IA), indolizinones (IB) and indolizinium (IC) ions are represented by the formulas:

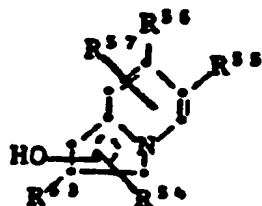
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-39-

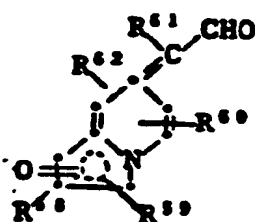
(IA)

5



10 (IB)

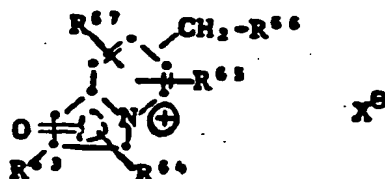
15



and

(IC)

20

 X^{\ominus}

25 wherein

X^{\ominus} is an anion as defined above;
 R^1 , R^2 , R^3 , R^4 , R^5 and
 R^6 are individually aryl containing 6 to
 14 carbon atoms, such as phenyl, naphthyl,
 anthryl, methoxyphenyl and methoxynaphthyl;
 aralkenyl containing 6 to 14 carbon atoms,
 such as 2,2-diphenylvinyl, 2-phenyl- vinyl,
 2-naphthylvinyl and 2-methyl-(2-phenyl-
 vinyl); alkyl containing 1 to 18 carbon
 atoms, such as methyl, ethyl, propyl, decyl
 and eicosyl; or R^1 and R^2 , R^3 and

-40-

$R^{5'}$, and $R^{6'}$ and $R^{6''}$ together represent the carbon atoms necessary to complete a 7- or 8-member cyclic structure;

$R^{5'}$, $R^{6'}$ and $R^{6''}$ are individually
 5 hydrogen, alkyl containing 1 to 18 carbon atoms, such as methyl, ethyl, and dodecyl; cyano; acyl containing 2 to 18 carbon atoms, such as acetyl, propionyl, 2-ethylhexanoyl and stearoyl; carboalkoxy
 10 containing 1 to 18 carbon atoms, such as carbomethoxy, carboethoxy and carbobutoxy; aminocarbonyl, such as unsubstituted aminocarbonyl, methylaminocarbonyl, dimethylaminocarbonyl and
 15 ethylaminocarbonyl; acyloxy containing 2 to 18 carbon atoms, such as acetoxy, propionoxy, butyroxoy and lauroyloxy; bromine and chlorine;

$R^{6'}$ is hydrogen; alkyl containing 1 to
 20 18 carbon atoms, such as methyl, ethyl, propyl and dodecyl; acyl containing 2 to 18 carbon atoms, such as acetyl, propionyl, butyryl and lauryl; benzyl or pyridyl;

$R^{5'}$, $R^{6'}$ and $R^{6''}$ are individually
 25 hydrogen; chlorine; bromine; or, alkyl containing 1 to 18 carbon atoms, such as methyl, ethyl, propyl and dodecyl;

$R^{6'}$ is alkyl containing 1 to 18 carbon
 30 atoms, such as methyl, ethyl, propyl, butyl and decyl; and

$R^{6''}$ is alkyl containing 1 to 18 carbon atoms; hydrogen; carbonyl; alkoxycarbonyl, such as methoxycarbonyl, ethoxycarbonyl and propoxycarbonyl; cyano; and carboxamido.

35 Such indolizins (IA), indolizinones (IB) and imidolizinium (IC) ions are prepared by reacting a cyclopropanone with a pyridine compound as described.

-41-

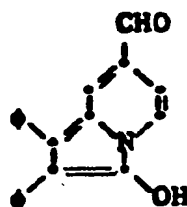
The term "active -CH= compounds" herein means aldehyde and ketone compounds which are capable of condensing with the active methylene of the indolizininium ion (IC) and which have

5 electropositive or electronegative substituents which complete a chromophore with the indolizininium ion (IC). The term "active -CH= compounds" includes active methylene compounds that are capable of condensing with indolizins (IA) or indolizinsones

10 (IB) to complete a chromophore. Examples of useful "active -CH= compounds" are as follows:

1,2-diphenyl-7-formyl-3-indolizinol

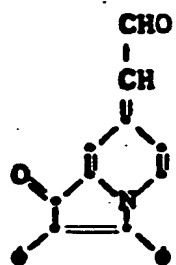
15



20

7-formylmethylidene-2,3-diphenyl-1(7H)-indolizinsonone

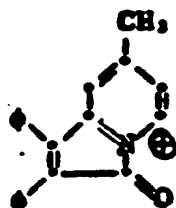
25



30

1,2-diphenyl-7-methyl-3-indolizininium trifluoromethane sulfonate

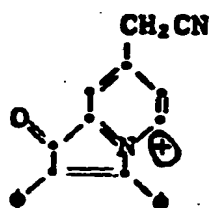
35

CF₃SO₃⁻

-42-

7-cyanomethyl-2,3-diphenyl-1-indolizininonium trifluoromethane sulfonate

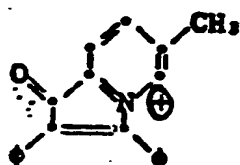
5

 CF_3SO_3^-

10

2,3-diphenyl-6-methyl-1-indolizininonium trifluoromethane sulfonate

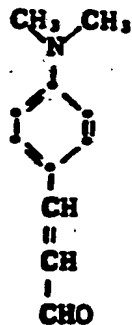
15

 CF_3SO_3^-

20

p-dimethylaminocinnamaldehyde

25



30

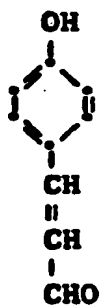
p-hydroxybenzaldehyde

35



p-hydroxycinnamaldehyde

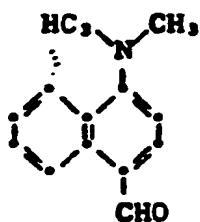
5



10

1-dimethylamino-4-formyl naphthalene

15



20

p-nitrobenzaldehyde

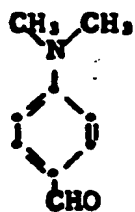
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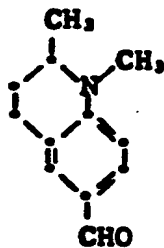
30

4-dimethylaminobenzaldehyde

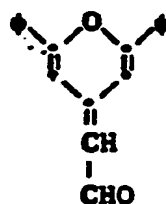
35



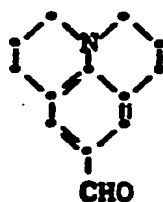
1,2-dimethyl-6-formyl-1,2,3,4-tetrahydroquinoline



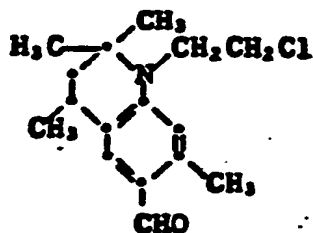
2,6-diphenyl-4-formylmethylenepyran (4H)pyran



9-formyljulolidene



1-chloroethyl-6-formyl-2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline



-45-

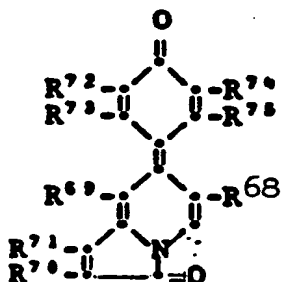
Many oxoindolizine dyes according to the invention are formed by the reaction of a phenolic coupler with an appropriate oxoindolizine. Examples of useful oxoindolizine dyes that are formed by
 5 reaction of phenolic couplers with a suitable oxoindolizine are represented by the formulas:

(XIII)

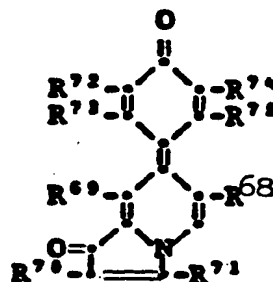
and

(XIV)

10



15



wherein:

20

R^{68} is hydrogen or a substituent that does not adversely affect desired dye properties, such as alkyl containing 1 to 18 carbon atoms; cyano; acyl containing 2 to 20 carbon atoms; carboalkoxy containing 2 to 18 carbon atoms; aminocarbonyl containing 1 to 18 carbon atoms; acyloxy containing 2 to 18 carbon atoms; bromine or chlorine;

25

30

R^{69} is hydrogen or a substituent that does not adversely affect desired dye properties, such as chlorine, bromine or alkyl containing 1 to 18 carbon atoms;

R^{70} and R^{71} are individually alkyl, containing 1 to 18, preferably 1 to 10 carbon atoms, or aryl containing 6 to 20 carbon atoms;

35

-46-

R⁷² and R⁷³ are individually hydrogen; alkyl containing 1 to 22 carbon atoms; aryl containing 6 to 20 carbon atoms; amino; carboxamido; sulfonamido; sulfamyl; carbamyl; halogen, including chlorine, fluorine, bromine and iodine; alkoxy containing 1 to 18 carbon atoms, or R⁷² and R⁷³ together represent the atoms necessary to complete a benzo group which is unsubstituted or substituted by at least one of the groups given above for R¹⁷; and

R⁷⁴ and R⁷⁵ are individually hydrogen; hydroxy; alkyl containing 1 to 22 carbon atoms; aryl containing 6 to 20 carbon atoms; amino; carboxamido; sulfonamido; sulfamyl; carbamyl; halogen, including chlorine, fluorine, bromine and iodine; or alkoxy containing 1 to 18 carbon atoms.

Examples of alkyl groups which are suitable for use as R⁶⁸ to and including R⁷⁵ substituents include, where conforming to the above carbon length descriptions, methyl, ethyl straight or branched chain propyl, butyl, decyl, dodecyl and eicosyl.

Acyl groups which are suitable for use as an R⁶⁸ substituent include acetyl, propionyl, 2-ethylhexanoyl and stearoyl.

Examples of carboalkoxy and aminocarbonyl groups which are suitable for use as an R⁶⁸ substituent include, respectively, carbomethoxy, carboethoxy and carbobutoxy, and unsubstituted aminocarbonyl or methylaminocarbonyl, dimethylaminocarbonyl, and ethylaminocarbonyl.

Acyloxy groups which are suitable for use as an R⁶⁸ substituent include acetoxy, propionoxy, butyroxy and lauroyloxy.

-47-

Examples of aryl groups which are suitable for use as R⁷⁰ to and including R⁷⁵ substituents are unsubstituted and substituted groups such as phenyl, tolyl, xylyl, methoxyphenyl,

5 4-t-butylphenyl, anisyl, naphthyl and methoxynaphthyl.

Examples of alkoxy groups which are suitable for use as R⁷² to and including R⁷⁵ substituents are methoxy, ethoxy and propoxy.

10 An example of a useful class of oxoindolizine dyes prepared from phenolic couplers are those derived from resorcinolic couplers. Resorcinolic couplers form compounds wherein R⁷³ is hydroxy.

15 Examples of oxoindolizine dyes prepared from phenolic couplers are as follows:

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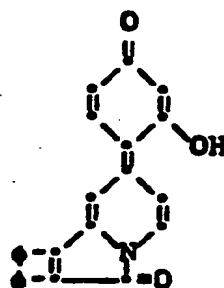
30

35

-48-

1,2-diphenyl-7-(4-oxo-2-hydroxy-1-phenylidene)-3(7H)-indolizinone

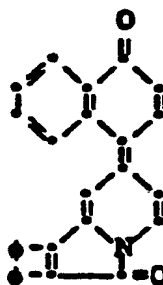
5



10

1,2-diphenyl-7-(4-oxo-1-naphthylidene)-3(7H)-indolizinone

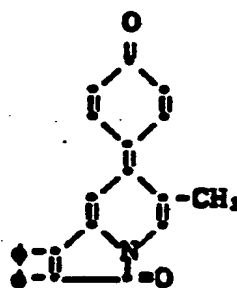
15



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1,2-diphenyl-6-methyl-7-(4-oxo-1-phenylidene)-3(7H)-indolizinone

25



30

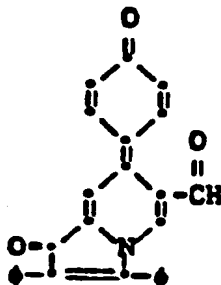
35

-49-

2,3-diphenyl-6-formyl-7-(4-oxo-1-phenylidene)-
1-(7H)-indolizinone

5

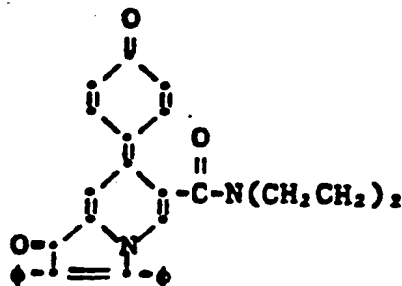
10



6-diethylaminocarbonyl-2,3-diphenyl-(4-
oxo-1-phenylidene)-1(7H)-indolizinone

15

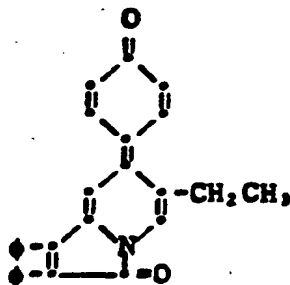
20



1,2-diphenyl-6-ethyl-7-(4-oxo-1-phenylidene)-
3(7H)-indolizinone

25

30



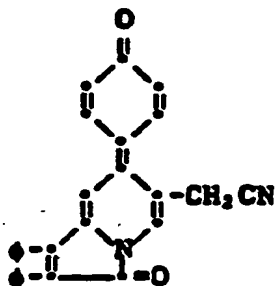
35

-50-

6-cyanomethyl-1,2-diphenyl-7-(4-oxo-1-phenylidene)-3(7H)-indolizinone

5

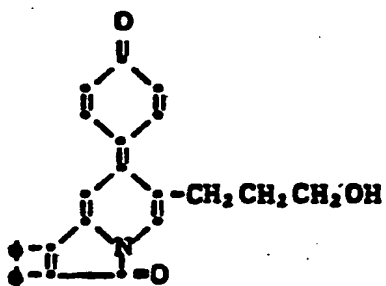
10



1,2-diphenyl-6-(3-hydroxypropyl)-7-(4-oxo-1-phenylidene)-3(7H)-indolizinone

15

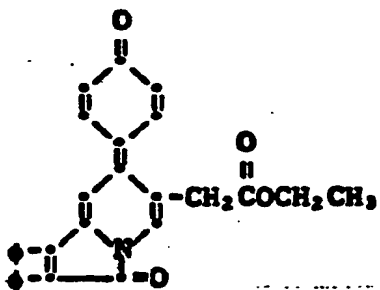
20



1,2-diphenyl-6-ethoxycarbonylmethyl-7-(4-oxo-1-phenylidene)-3(7H)-indolizinone

25

30

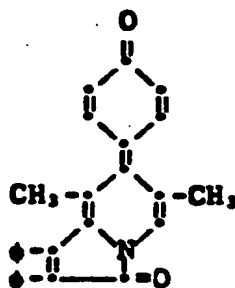


35

-51-

6,8-dimethyl-1,2-diphenyl-7-(4-oxo-1-phenylidene)-3(7H)-indolizinone

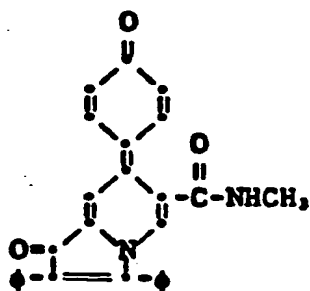
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2,3-diphenyl-6-methylaminocarbonyl-7-(4-oxo-1-phenylidene)-1(7H)-indolizinone

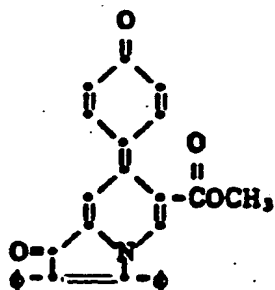
15



20

2,3-diphenyl-6-methoxycarbonyl-7-(4-oxo-1-phenylidene)-1(7H)-indolizinone

25



30

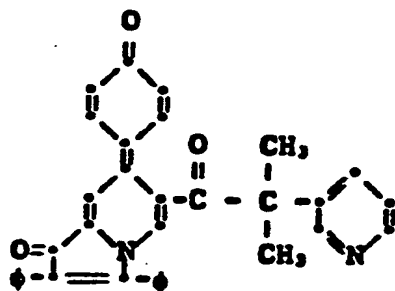
35

-52-

2,3-diphenyl-6-[2-methyl-2-(3-pyridyl)-
propionyl-7-(4-oxo-1-phenylidene)]-1(7H)-
indolizinone

5

10

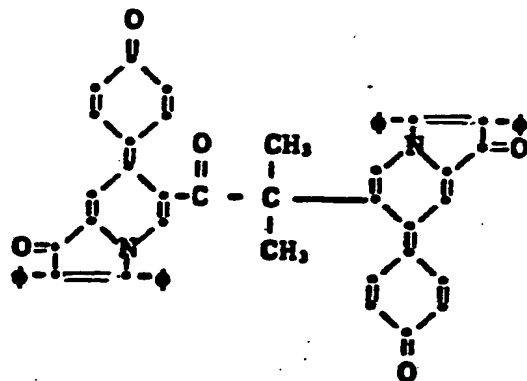


15

1,2-bis[6,6'-[2,3-diphenyl-7-(4-oxo-1-
phenylidene)-1(7H)-indolizinonyl]]-2-
methyl-1-oxopropane

20

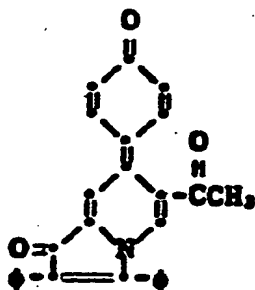
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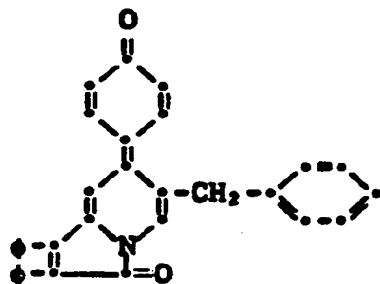
6-acetyl-2,3-diphenyl-7-(4-oxo-phenyl-
idene)-1(7H)-indolizinone

35

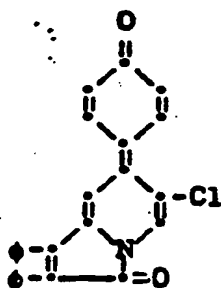


-53-

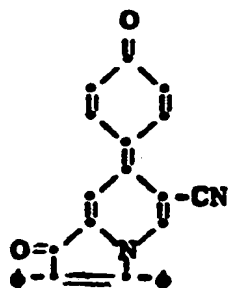
**6-benzyl-1,2-diphenyl-7-(4-oxo-1-phenyl-
idene)-3(7H)-indolizinone**



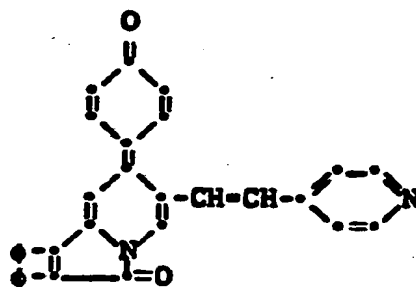
**6-chloro-1,2-diphenyl-7-(4-oxo-1-phenyl-
idene)-3(7H)-indolizinone**



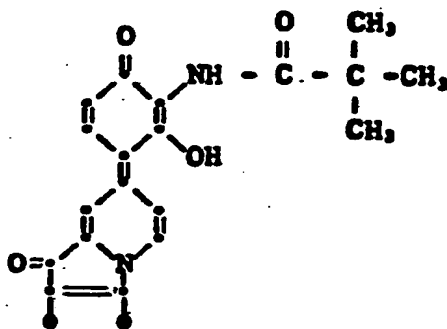
**6-cyano-2,3-diphenyl-7-(4-oxo-1-phenyl-
idene)-1(7H)-indolizininone**



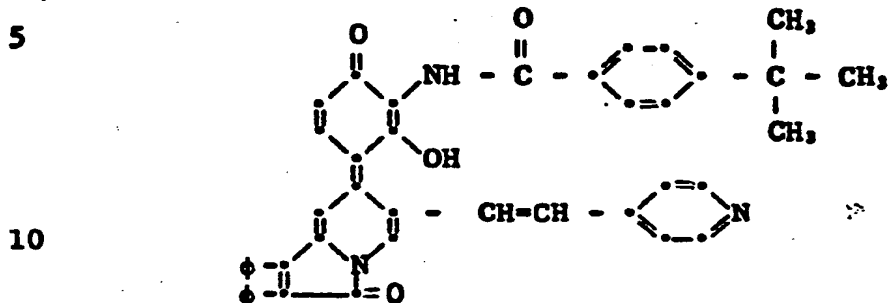
6-(4-azastyryl)-1,2-diphenyl-7-(4-oxo-1-phenylidene)-3(7H)-indolizinone



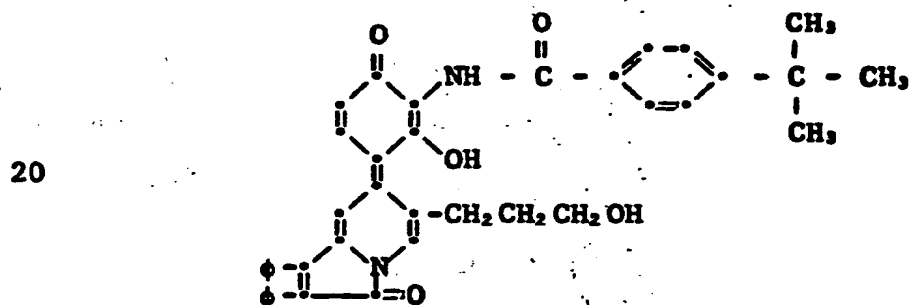
2,3-diphenyl-7-(2-hydroxy-4-oxo-3-pival-amido-1-phenylidene)-1(7H)-indolizinone



6-(4-azastyryl)-7-[3-(4-tert-butylbenz-
amido)-2-hydroxy-4-oxo-1-phenylidene]-1,2-
diphenyl-3(7H)-indolizinone

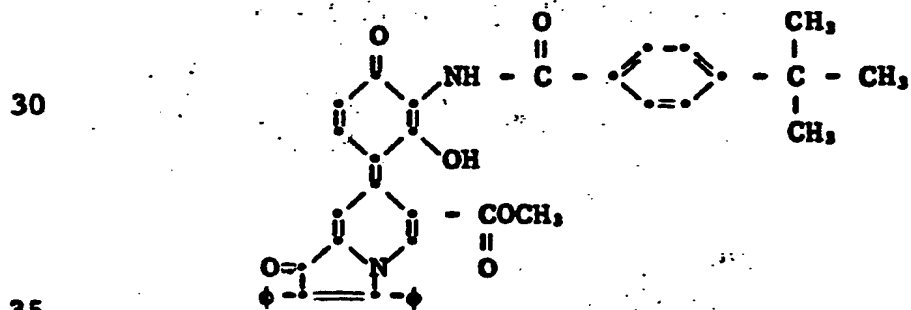


7-[3-(4-tert-butylbenzamido)-2-hydroxy-
4-oxo-1-phenylidene]-1,2-diphenyl-6-(3-
hydroxypropyl)-3(7H)-indolizinone



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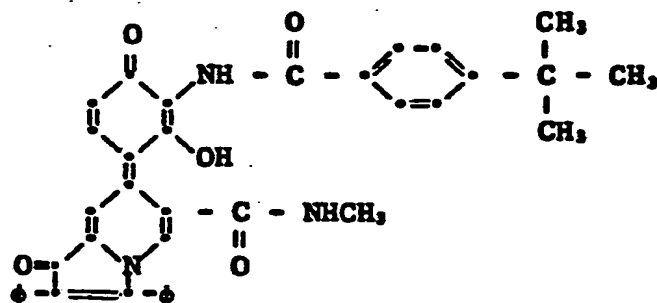
7-[3-(4-tert-butylbenzamido)-2-hydroxy-
4-oxo-1-phenylidene]-6-carbomethoxy-2,3-
diphenyl-1(7H)-indolizinone



7-[3-(4-tert-butylbenzamido)-2-hydroxy-4-oxo-1-phenylidene]-2,3-diphenyl-6-methyl-carbamyl-1(7H)-indolizininone

5

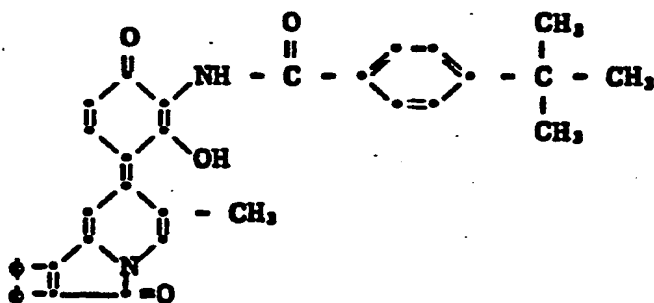
10



15

7-[3-(4-tert-butylbenzamido)-2-hydroxy-4-oxo-1-phenylidene]-1,2-diphenyl-6-methyl-3(7H)-indolizininone

20

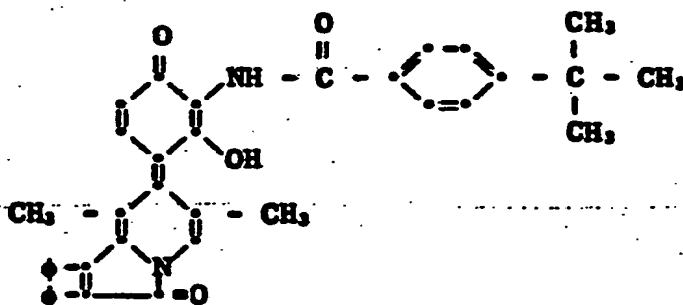


25

7-[3-(4-tert-butylbenzamido)-2-hydroxy-4-oxo-1-phenylidene]-6,8-dimethyl-1,2-diphenyl-3(7H)-indolizininone

30

35

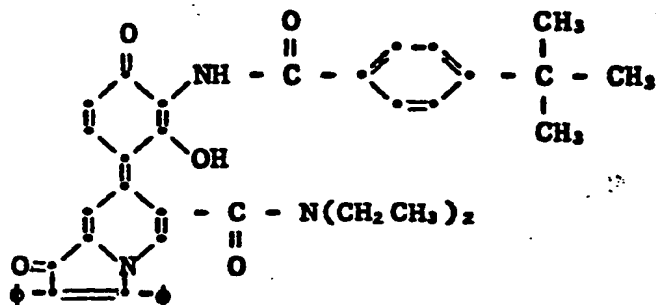


-57-

7-[3-(4-tert-butylbenzamido)-2-hydroxy-4-oxo-1-phenylidene]-6-diethylcarbamyl-2,3-diphenyl-1(7H)-indolizinone

5

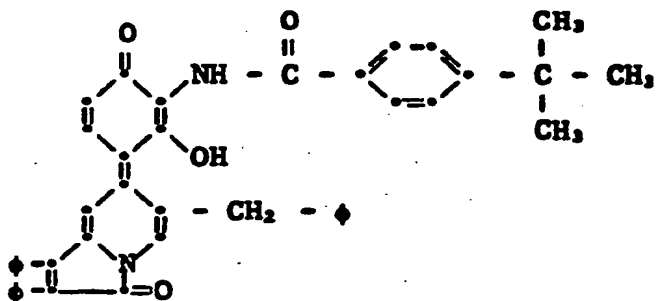
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15

6-benzyl-7-[3-(4-tert-butylbenzamido)-2-hydroxy-4-oxo-1-phenylidene]-1,2-diphenyl-3(7H)-indolizinone

20



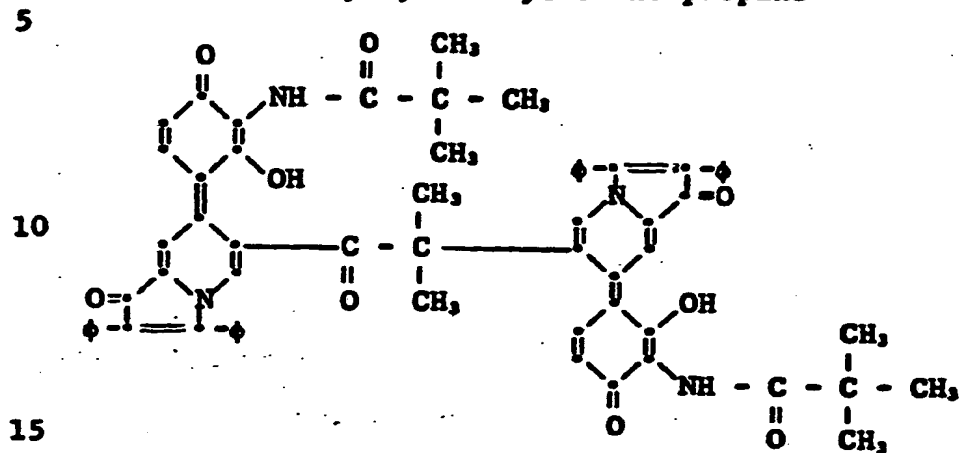
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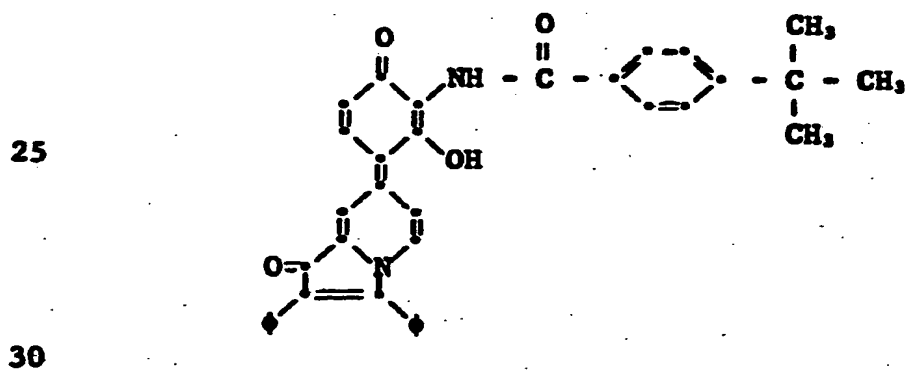
-58-

1,2-bis-[6,6'-{7-[3-(4-tert-butylbenzamido)-2-hydroxy-4-oxo-1-phenylidene]}-2,3-diphenyl-1(7H)-indoliz-
 zinonyl-}2-methyl-1-oxo-propane



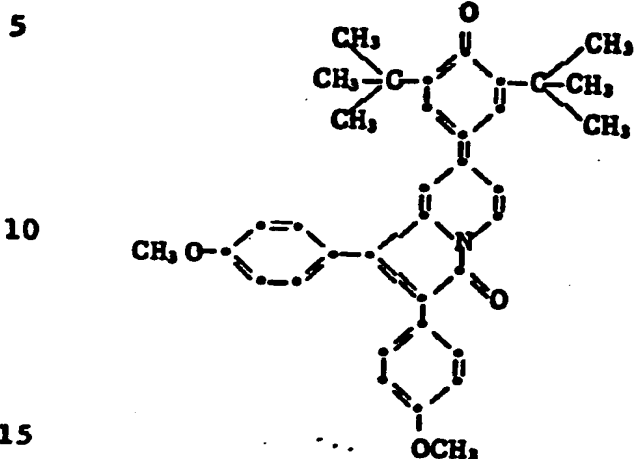
20

2,3-diphenyl-7-[3-(4-tert-butylbenzamido)-
 2-hydroxy-4-oxo-1-phenylidene]-1(7H)-
 indolizinone

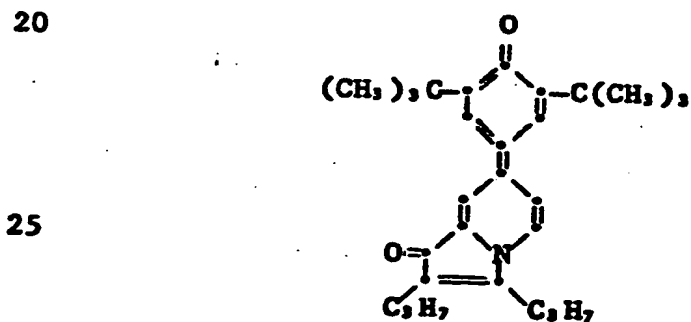


35

7-[3,5-di-tert-butyl-4-oxo-1-phenylidene]-
1,2-di-(4-methoxyphenyl)-3(7H)-indolizininone



7-[3,5-di-tert-butyl-4-oxo-1-phenylidene]-
2,3-di-n-propyl-1(7H)-indolizininone

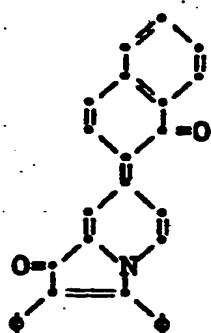


Further examples of oxoindolizine dyes
30 prepared from phenolic couplers are listed below.
Where available, λ_{max} values, in nanometers (nm),
are reported in parentheses:

35

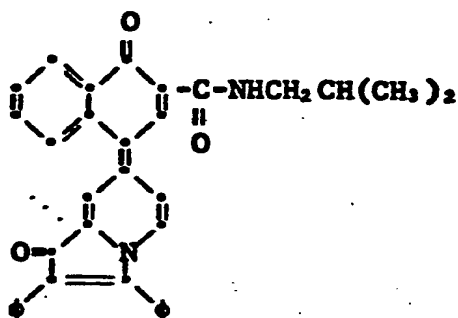
-60-

5



(750)

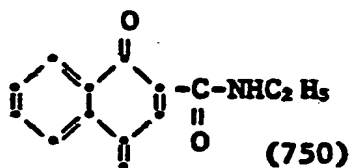
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(750)

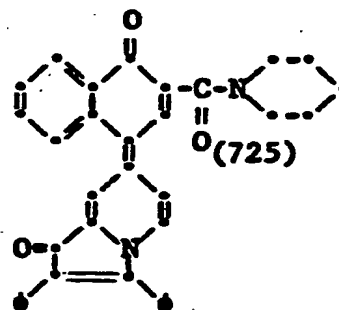
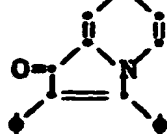
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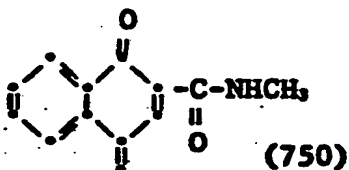
(750)

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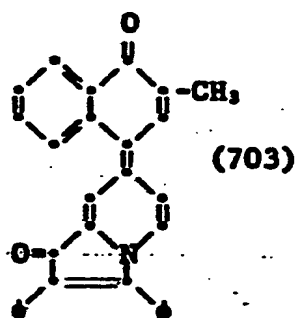
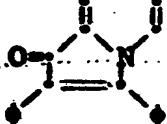
(725)

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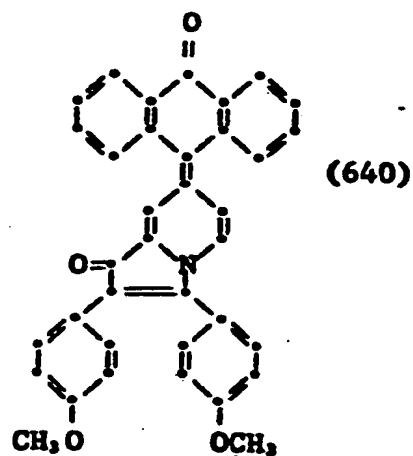
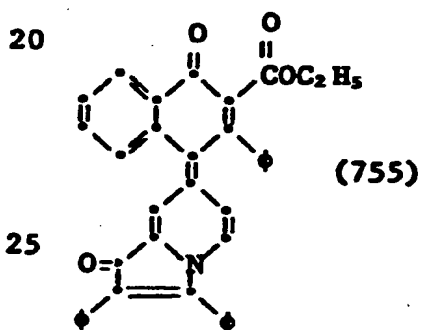
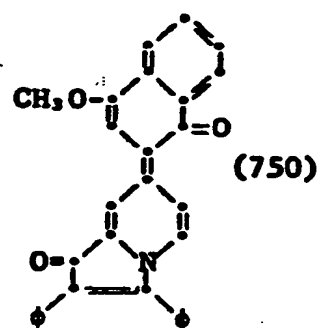
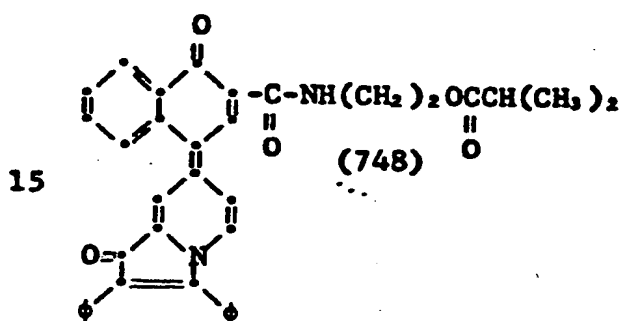
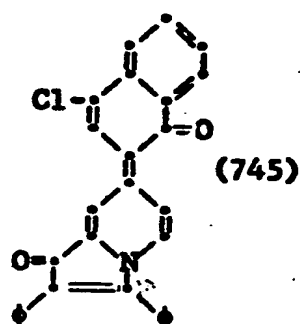
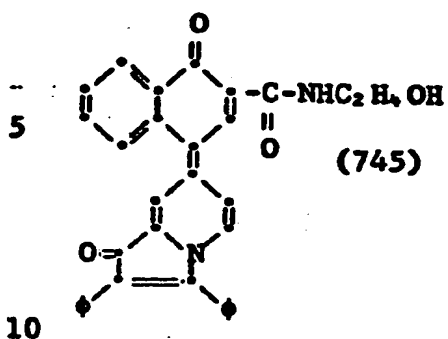


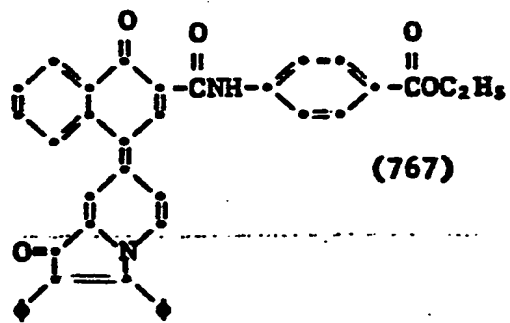
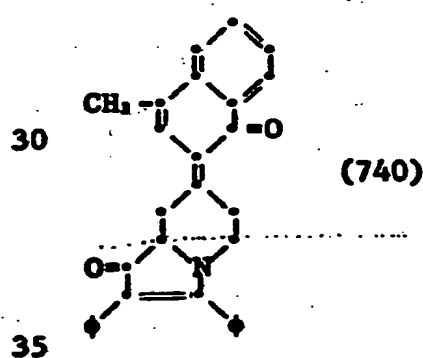
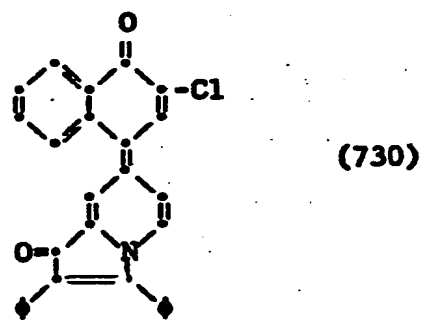
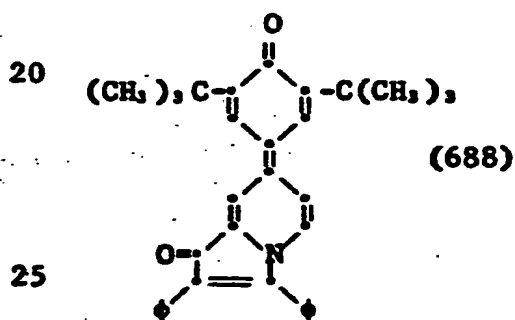
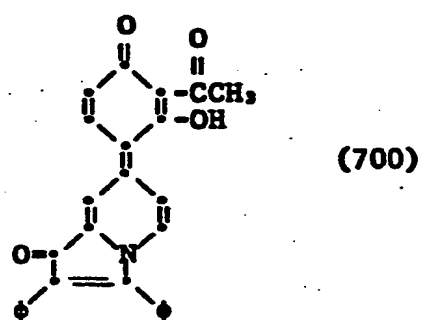
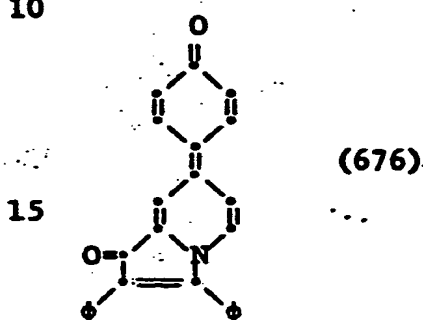
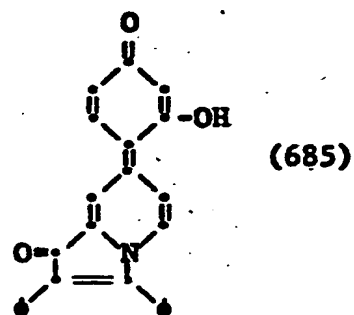
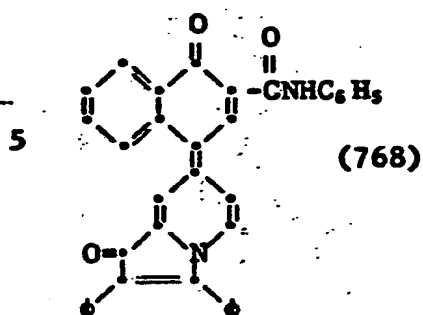
(750)

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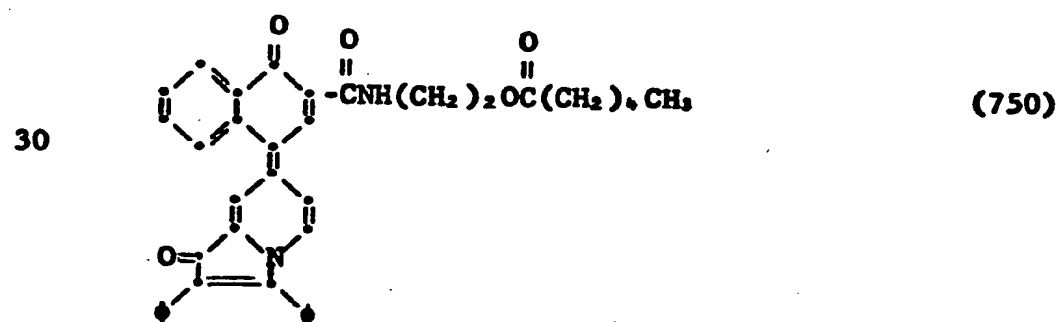
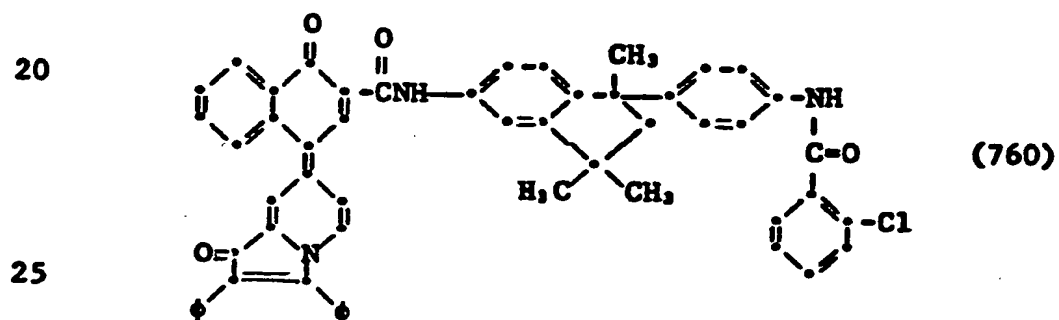
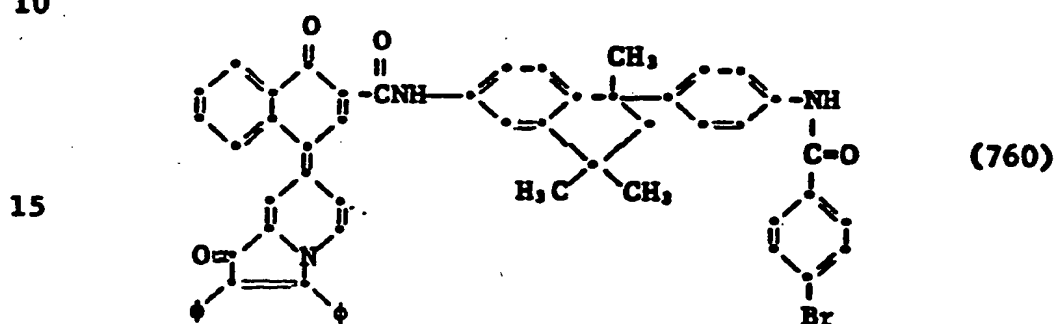
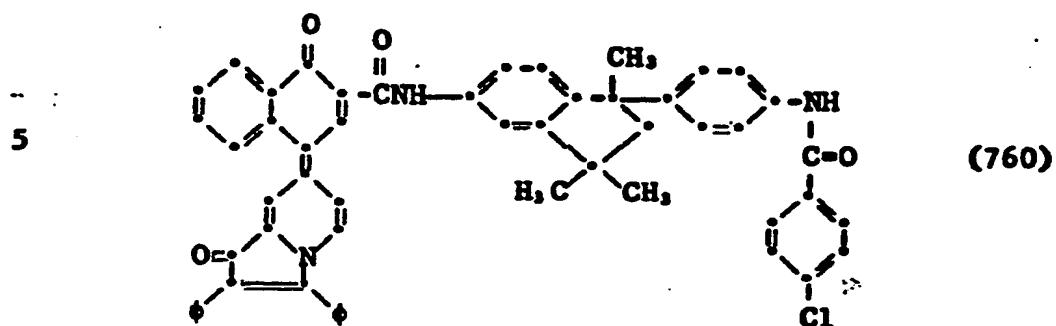
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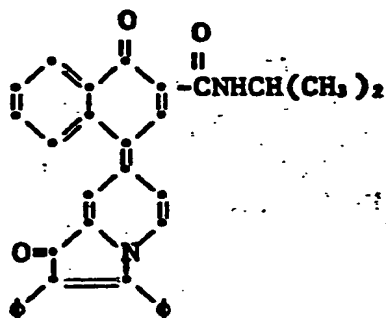




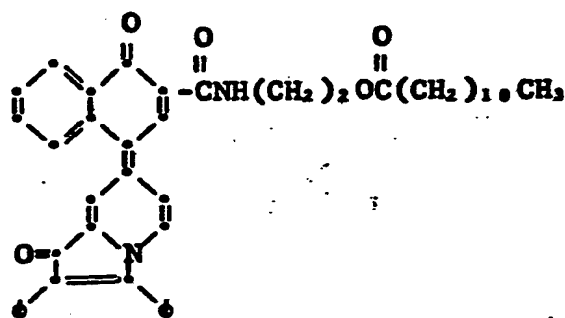
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-63-





(750)



(750)

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Oxoindolizinium dyes according to the invention are also formed from reaction of an aniline coupler with an oxoindolizine compound. Such dyes are represented by the structural formulae:

25

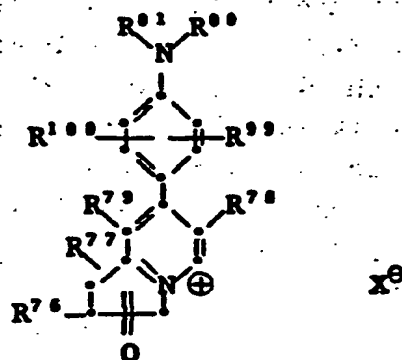
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(XV)

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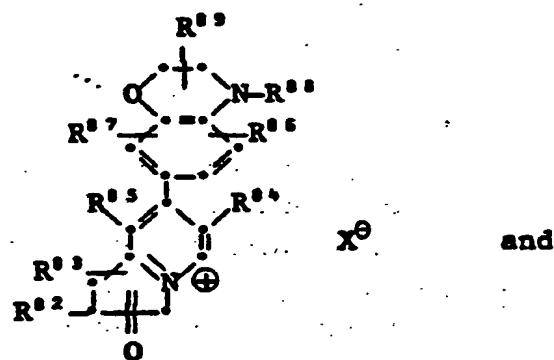
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(XVI)

15

20

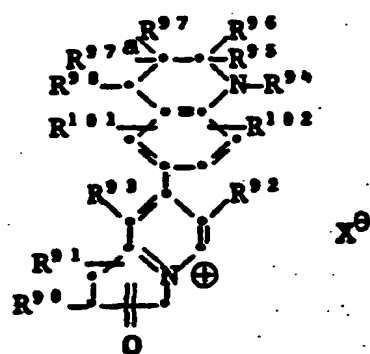


and

(XVII)

25

30



wherein

35

-66-

$R^{7'6}$, $R^{7'7}$, $R^{8'2}$, $R^{8'3}$, $R^{8'8}$ and $R^{9'1}$ are individually aryl containing 6 to 14 carbon atoms, such as phenyl, naphthyl, anthryl, methoxyphenyl and methoxynaphthyl; aralkenyl containing 6 to 14 carbon atoms, such as 2,2-diphenylvinyl, 2-phenyl-vinyl, 2-naphthylvinyl and 2-methyl-(2-phenyl-vinyl); alkyl containing 1 to 18 carbon atoms, such as methyl, ethyl, propyl, decyl and eicosyl; or $R^{7'6}$ and $R^{7'7}$, $R^{8'2}$ and $R^{8'3}$, $R^{8'8}$ and $R^{9'1}$ together represent the carbon atoms necessary to complete a 7- or 8-member cyclic structure,

$R^{7'8}$, $R^{8'4}$ and $R^{9'2}$ are individually hydrogen, alkyl containing 1 to 18 carbon atoms, such as methyl, ethyl, and dodecyl; cyano; acyl containing 2 to 18 carbon atoms, such as acetyl, propionyl, 2-ethylhexanoyl and stearoyl; carboalkoxy containing 2 to 18 carbon atoms such as carbomethoxy, carboethoxy and carbobutoxy; aminocarbonyl, methylaminocarbonyl, dimethylaminocarbonyl and ethylamino-carbonyl; acyloxy containing 2 to 18 carbon atoms, such as acetoxo, propionoxo, butyroxo and lauroyloxy; bromine and chlorine;

$R^{7'9}$, $R^{8'5}$ and $R^{9'3}$ are individually hydrogen; chlorine; bromine; or, alkyl containing 1 to 18 carbon atoms, such as methyl, ethyl, propyl and dodecyl;

$R^{8'6}$, $R^{8'1}$, $R^{8'8}$ and $R^{9'4}$ are individually hydrogen or substituents that do not adversely affect the desired indolizinium dye, such as alkyl containing 1 to 18 carbon atoms, such as methyl,

-67-

ethyl, propyl, decyl, and lauryl;
 cycloalkyl, such as cycloalkyl containing 6
 to 20 carbon atoms; straight or branched
 chain alkenyl containing 2 to 10 carbon
 atoms; or R^{10} and R^{11} together
 represent the atoms necessary to complete a
 5- or 6-member heterocyclic ring with the
 nitrogen atom to which they are bonded,
 such as atoms completing a pentamethylene,
 ethyleneoxyethylene or ethylenesulfonyl-
 ethylene group which forms a ring, or a
 julolidyl group;

R^{12} , R^{13} , R^{14} , R^{15} , R^{16} and
 R^{17} are individually hydrogen; fluorine;
 chlorine; bromine; alkyl containing 1 to 6
 carbon atoms; cycloalkyl containing 5 to 12
 carbon atoms; alkoxy containing 1 to 4
 carbon atoms; phenoxy; alkylthio, such as
 alkylthio containing 1 to 4 carbon atoms;
 arylthio, such as arylthio containing 6 to
 20 carbon atoms; and groups represented by
 the formula $-NH-XR^{18}$ in which X is $-CO-$,
 $-COO-$ or $-SO_2-$, wherein R^{18} is as
 defined above; and

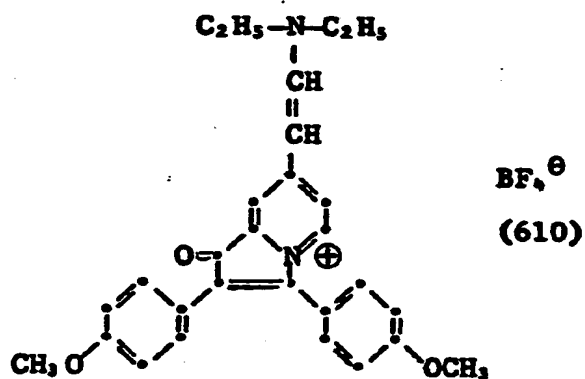
R^{19} , R^{20} , R^{21} , R^{22} , R^{23} and
 R^{24} are individually hydrogen and alkyl
 containing 1 to 6 carbon atoms; and
 X^{\ominus} is an anion as defined above,
 such as $CF_3SO_3^{\ominus}$, BF_4^{\ominus} and
 Br^{\ominus} .

Examples of related oxoindolizinium and
 oxoindolizine dyes are:

7-(2-N,N-diethylamino-1-ethenyl)-2,3-di-(4-methoxyphenyl)-1-oxoindolizinium fluoborate

5

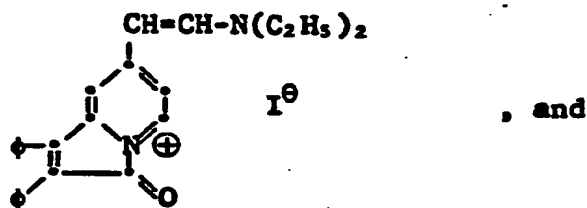
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15

7-(2-N,N-diethylamino-1-ethenyl)-1,2-diphenyl-3-oxoindolizinium iodide

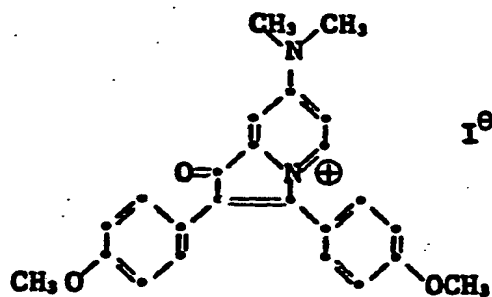
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25

2,3-di-(4-methoxyphenyl)-7-dimethylamino-1-oxoindolizinium iodide

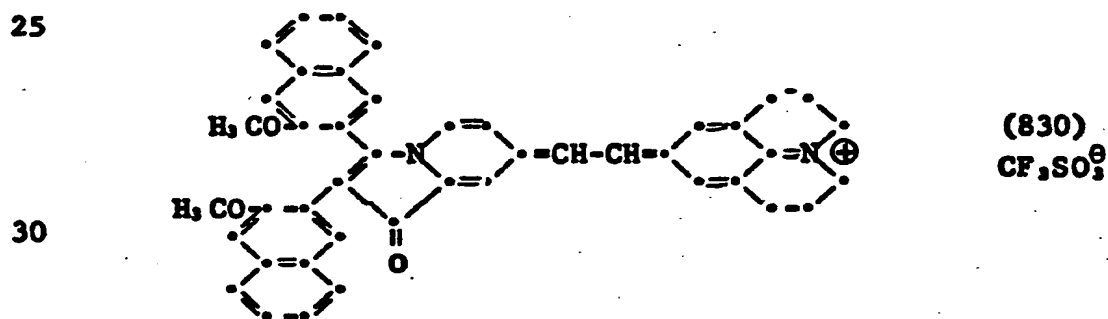
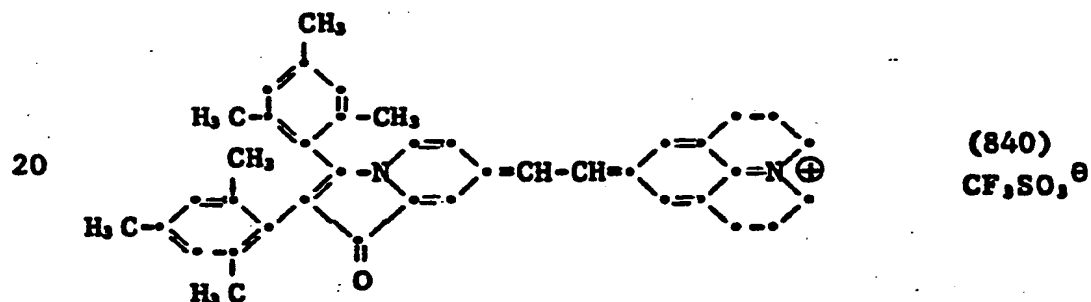
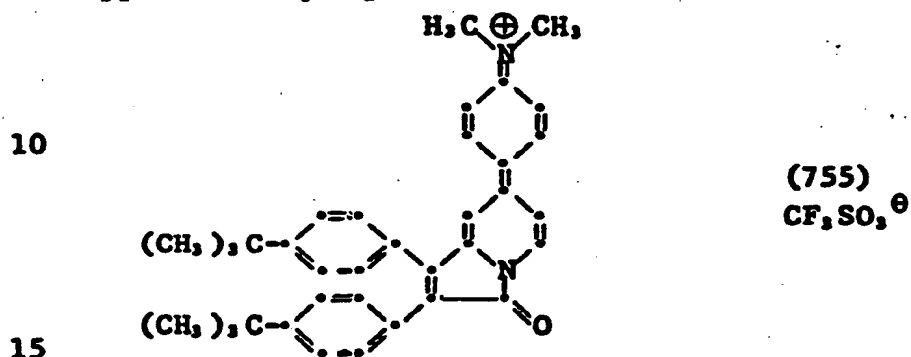
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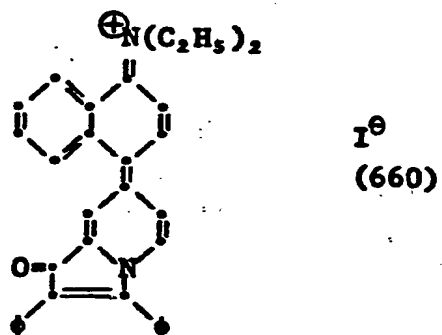
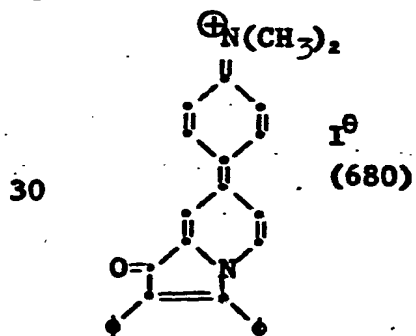
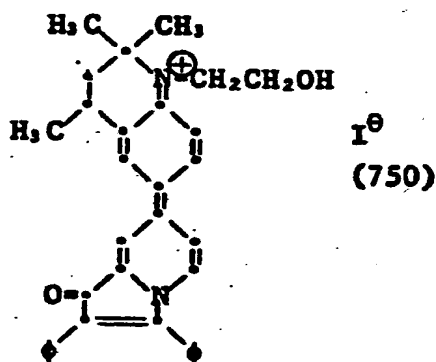
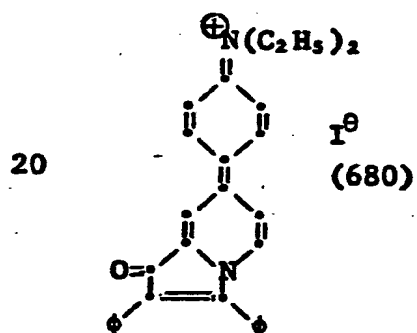
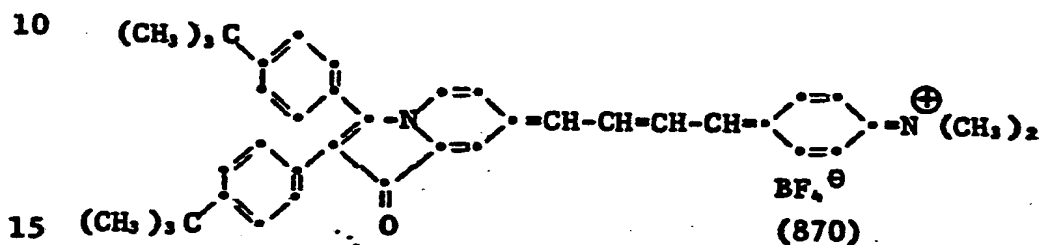
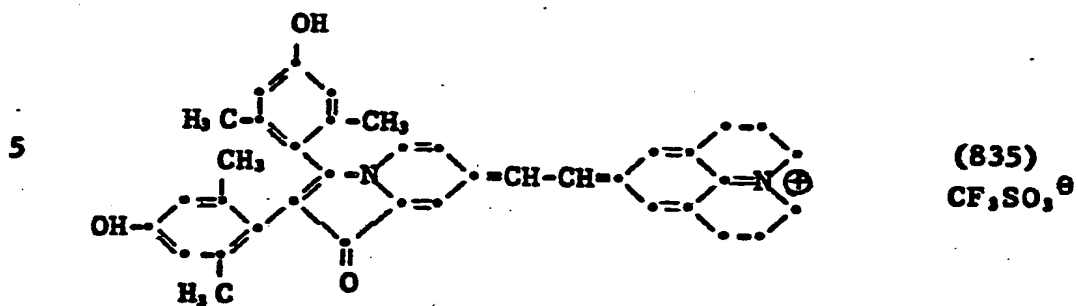
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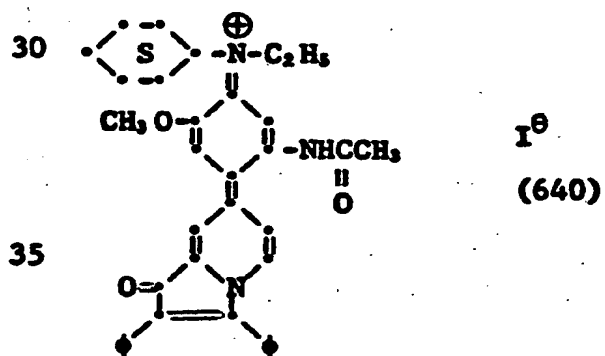
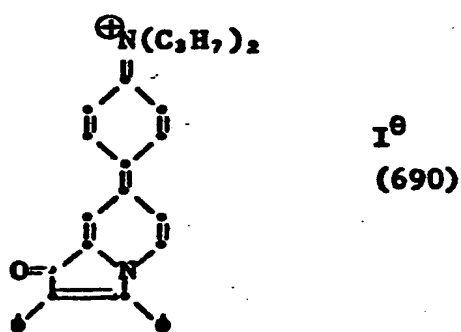
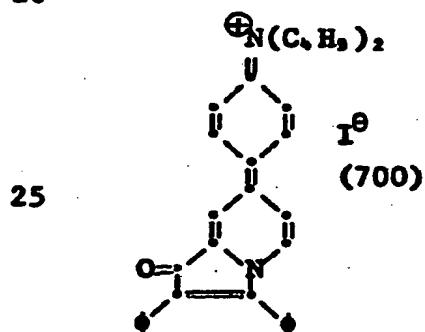
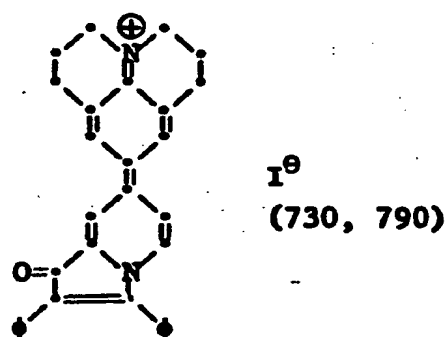
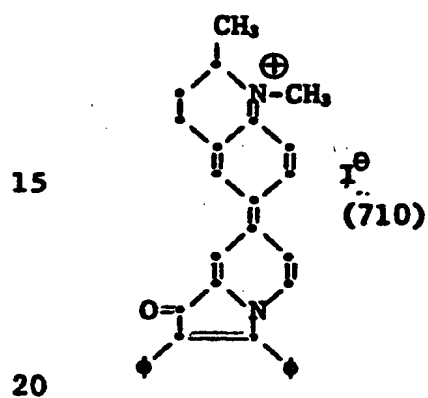
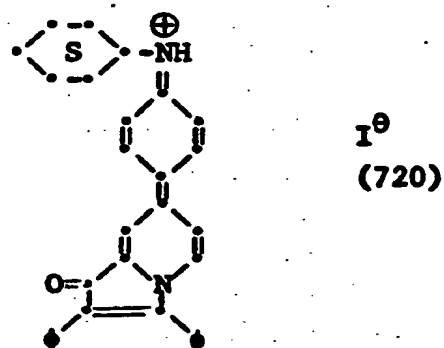
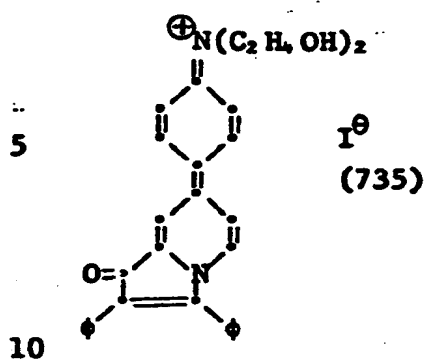
-69-

Further examples of oxoindolizinium dyes are listed below. Where available, λ_{max} values, in nanometers (nm), are reported in parentheses. In instances where two λ_{max} values are reported, both value intensities are approximately equal.



35





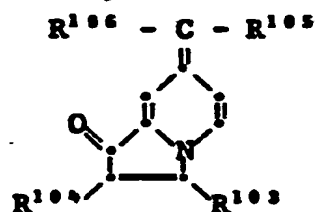
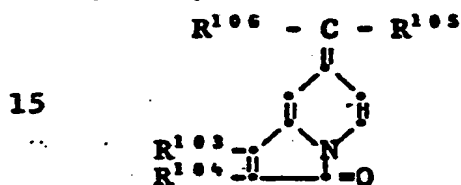
-72-

Many useful oxoindolizine dyes according to the invention are formed from the reaction of an active methylene coupler with a suitable oxoindolizine compound. Especially useful oxoindolizines are dyes formed from the reaction of ketomethylene couplers, methylpyrylium couplers and methylindolizinium couplers with appropriate oxoindolizine compounds. Examples of useful indolizine dyes formed from active methylene couplers are represented by the formula:

(XVIII)

and

(XVIII A)



wherein:

20 R^{103} and R^{104} are individually aryl containing 6 to 20 carbon atoms, such as phenyl, naphthyl, anthryl, methoxyphenyl and methoxynaphthyl; aralkenyl containing 6 to 20 carbon atoms, such as
25 2,2-diphenylvinyl, 2-phenylvinyl, 2-naphthylvinyl and 2-methyl-(2-phenylvinyl); alkyl containing 1 to 18 carbon atoms, such as methyl, ethyl, propyl, decyl and lauryl; or R^{103} and R^{104} together represent the carbon atoms necessary to complete a 7- or
30 8-member cyclic structure;

35 R^{105} and R^{106} are individually electronegative groups, such as aryl containing 6 to 20 carbon atoms, such as phenyl and naphthyl; cyano; acyl containing

-73-

2 to 18 carbon atoms, such as acetyl, propionyl and butyryl; carboalkoxy containing 2 to 18 carbon atoms, such as carbomethoxy, carboamyloxy and carbobutoxy; aminocarbonyl containing 2 to 18 carbon atoms such as unsubstituted aminocarbonyl, methylaminocarbonyl, dimethylaminocarbonyl and ethylaminocarbonyl; and R^{108} is alternatively hydrogen.

Examples of oxoindolizine dyes formed from active methylene couplers are shown below. Where available, λ_{\max} values, in nanometers (nm), are reported in parentheses:

15

20

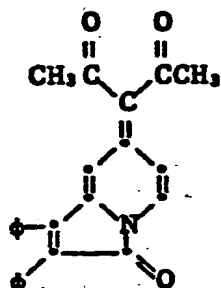
25

30

35

7-(diacetylmethylidene)-1,2-diphenyl-3-(7H)-indolizine

5

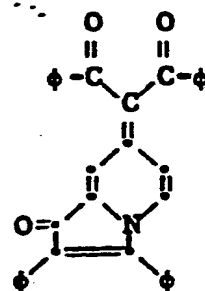


(410, 480)

10

7-(dibenzoylmethylidene)-2,3-diphenyl-1-(7H)-indolizine

15



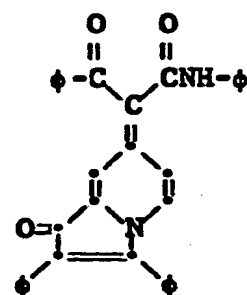
(610)

20

25

7-(anilinocarbonyl benzoylmethylidene)-2,3-diphenyl-1(7H)-indolizine

30

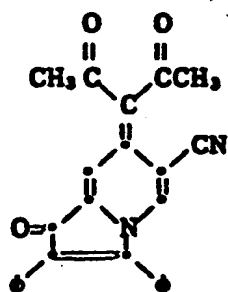


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-75-

6-cyano-7-(diacetylmethylidene)-2,3-diphenyl-1(7H)-indolizinone

5

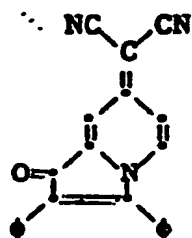


(530)

10

7-(dicyanomethylidene)-2,3-diphenyl-1(7H)-indolizinone

15

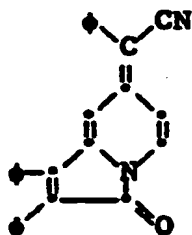


(555, 590)

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7-(1-cyano-1-phenylmethylidene)-1,2-diphenyl-3(7H)-indolizinone

25

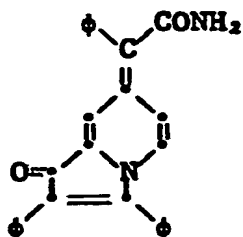


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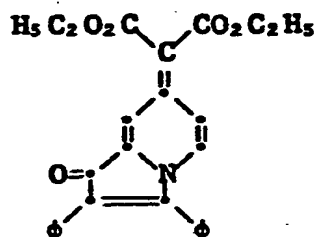
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-76-

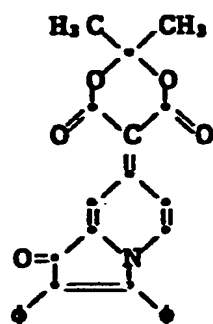
7-(1-aminocarbonyl-1-phenylmethylidene)-
2,3-diphenyl-1(7H)-indolizinone



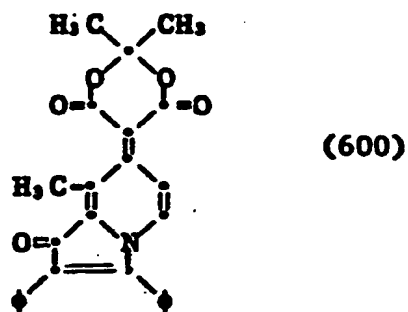
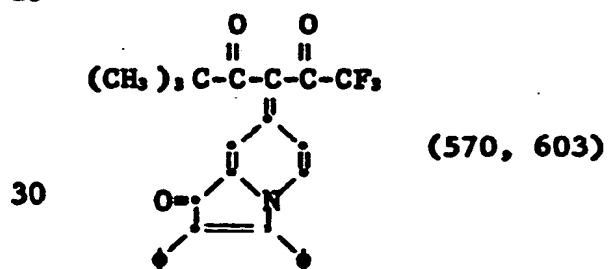
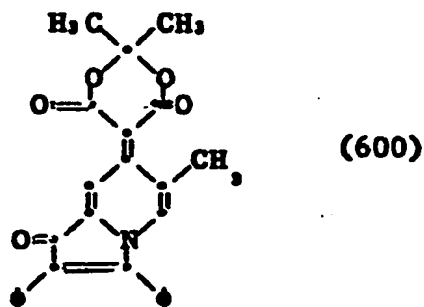
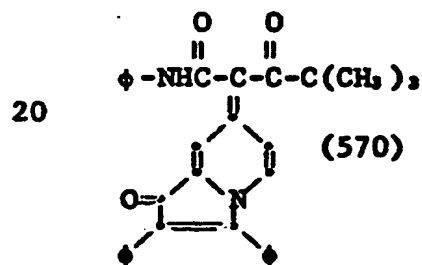
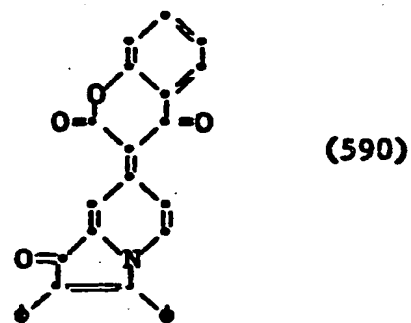
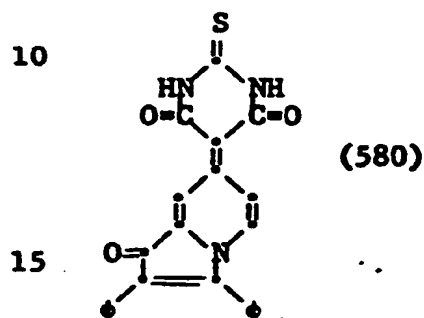
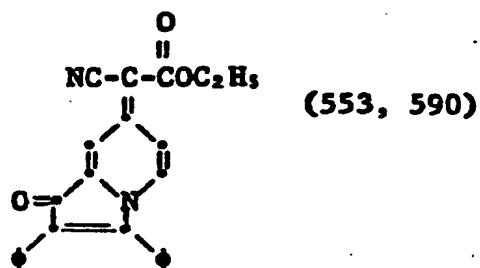
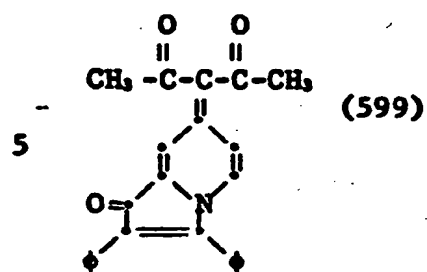
7-(dicarboethoxymethylidene)-2,3-diphenyl-
1(7H)-indolizinone

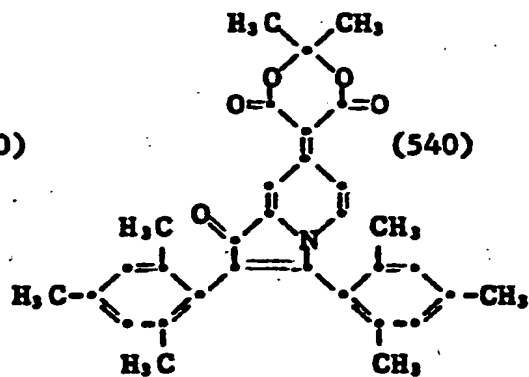
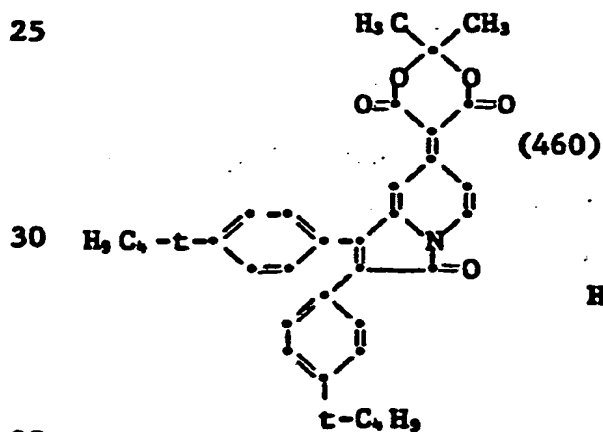
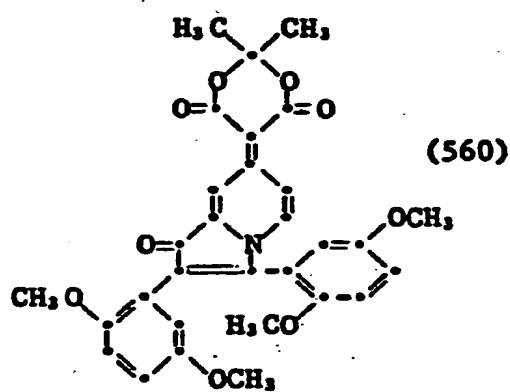
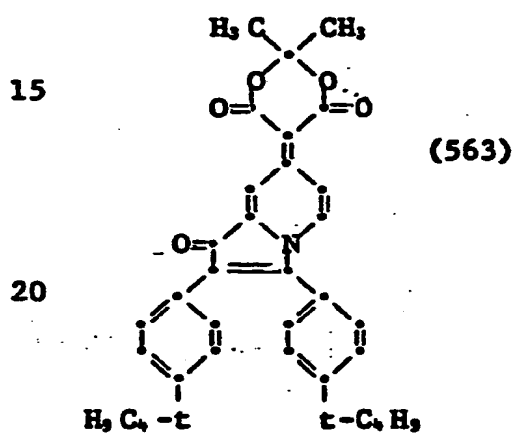
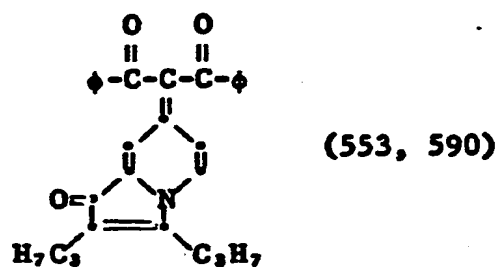
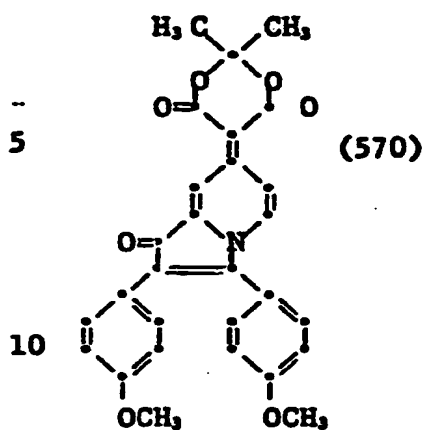


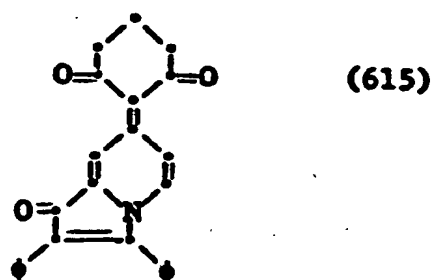
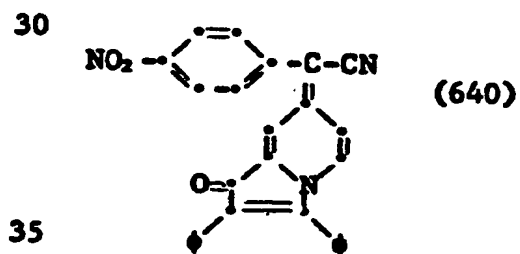
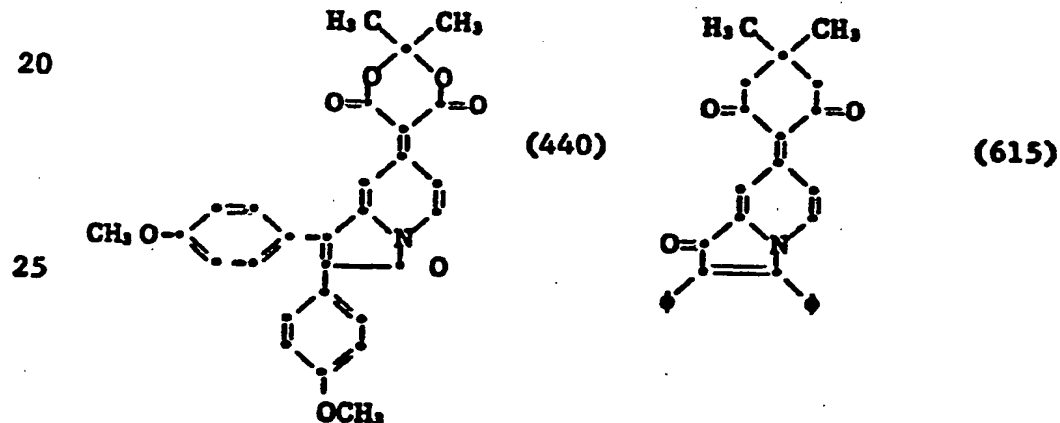
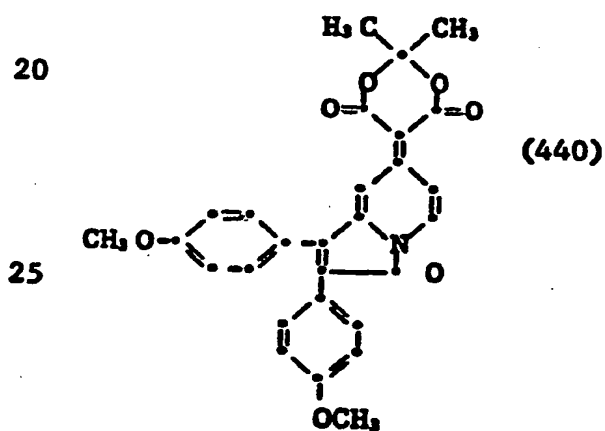
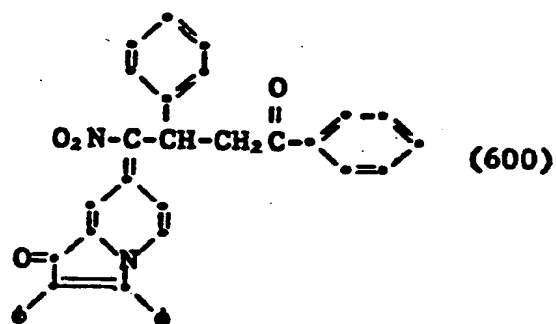
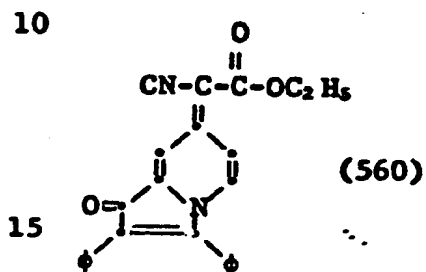
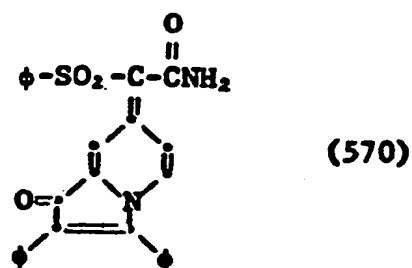
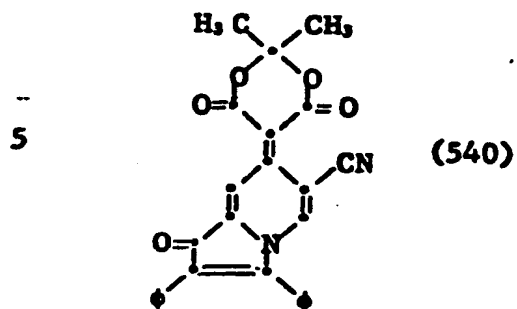
2,3-diphenyl-7-(2,2-dimethyl-4,6-dioxo-
1,3-dioxanylidene)-1(7H)-indolizinone

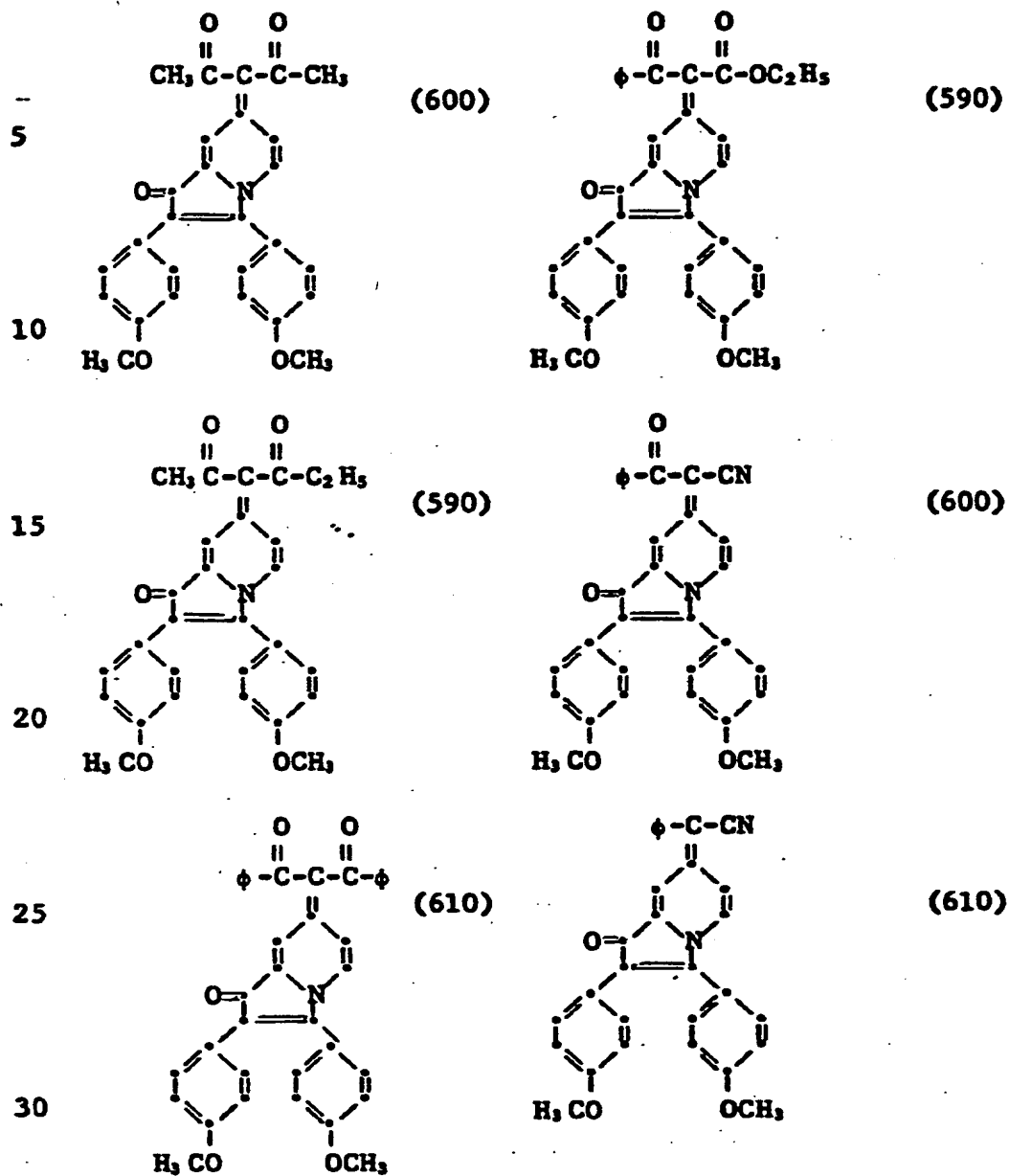


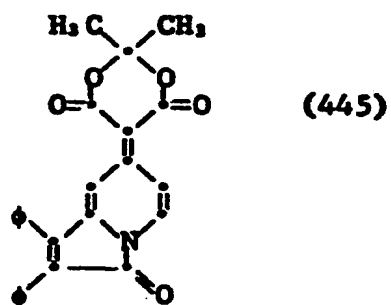
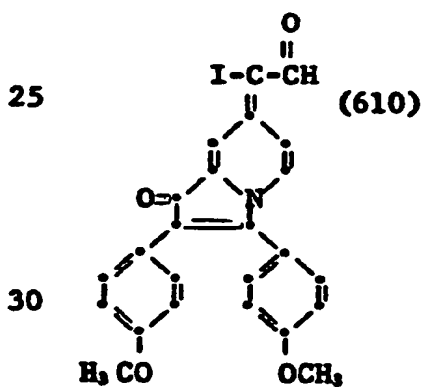
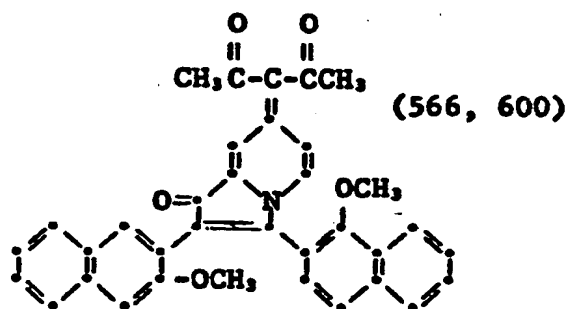
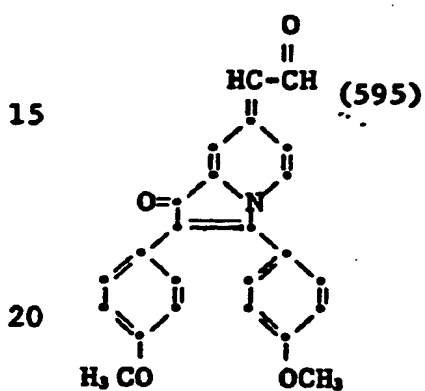
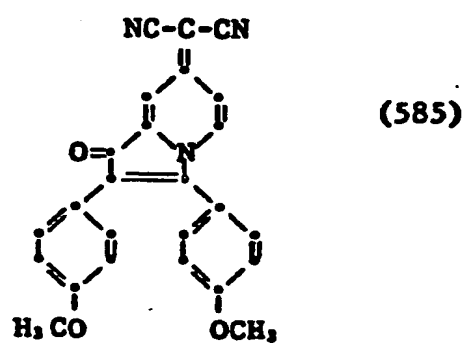
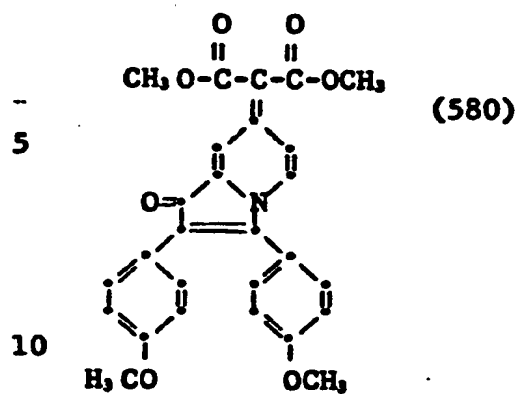
(560, 580)

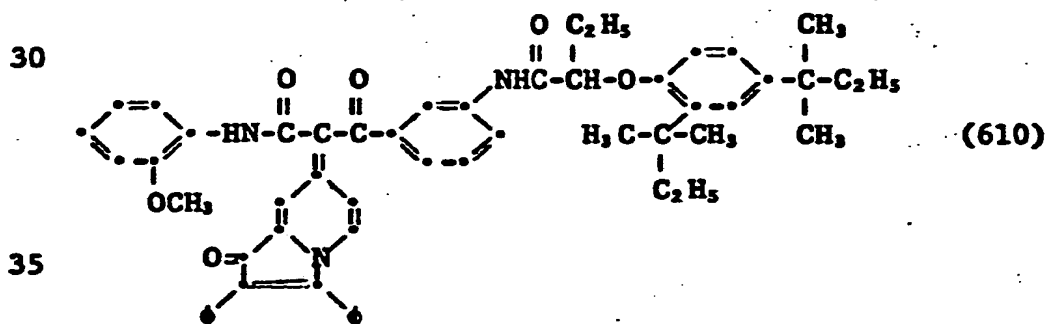
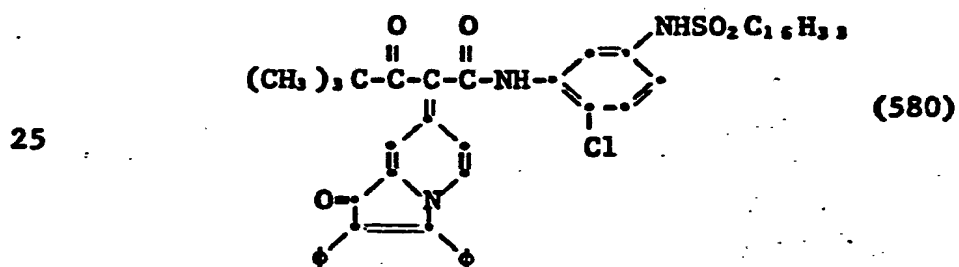
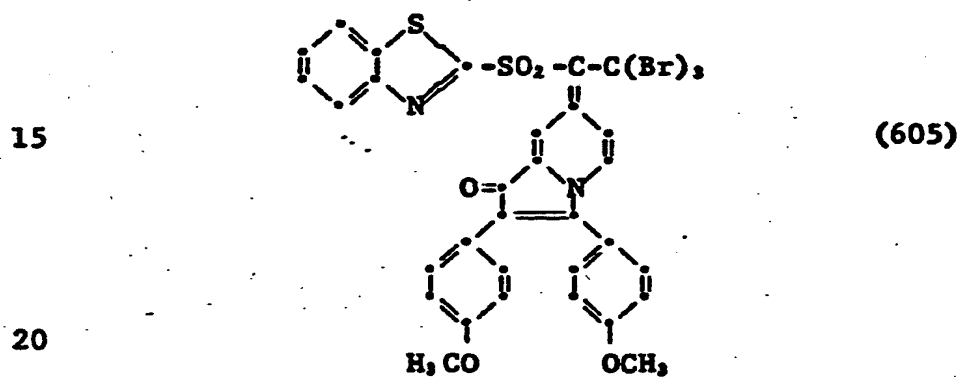
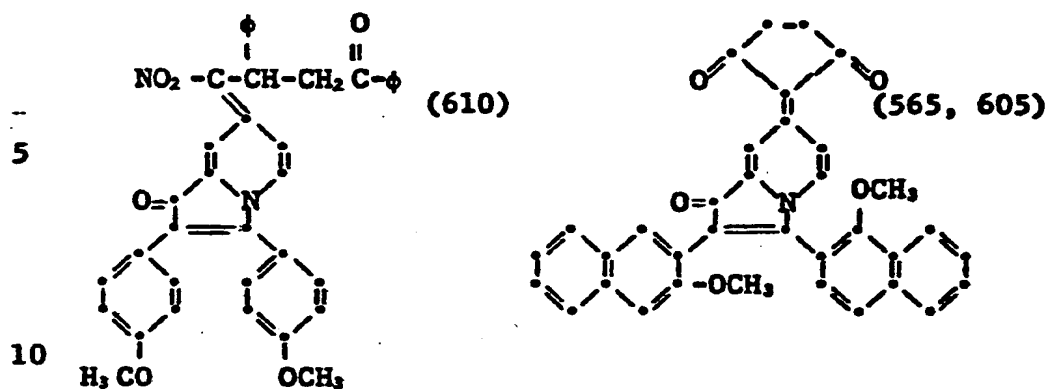








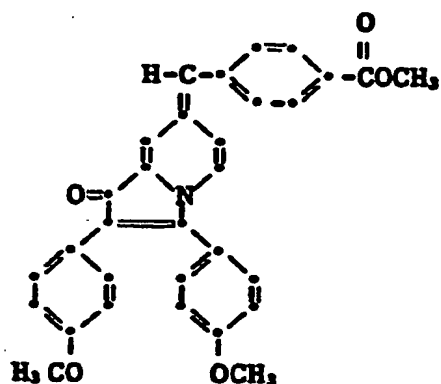




-83-

5

10



(615)

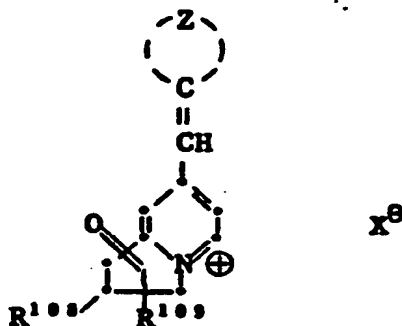
Examples of oxoindolizinium dyes
formed from active methylene couplers are
represented by the formula:

15

(XIX)

20

25



wherein

30

X^{\ominus} is an anion as defined above;
 R^{100} and R^{100} are individually the
same as R^{100} and R^{100} ; and

35

Z represents the atoms necessary to
complete a chromophore, such as the carbon,
hydrogen, oxygen and nitrogen atoms
necessary to complete a heterocyclic group,
such as a pyranilidene, indolizinylidene,

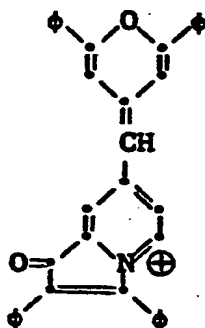
-84-

thiopyranylidene, selenopyranylidene,
coumarinylidene, or pyrazolinonylidene
group.

5 Examples of oxoindolizinium dyes formed
from such active methylene couplers are as follows:

2,3-diphenyl-7-[(2,6-diphenyl-4-
pyranylidene)methyl]-1-oxoindolizinium
perchlorate

10

 ClO_4^-

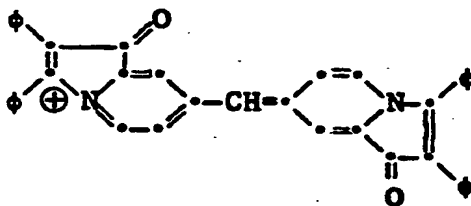
(695)

15

20

2,3-diphenyl-7-[(2,3-diphenyl-7-1(7H)-
indolizinonylidene)methyl]-1-indoli-
zinonium trifluoromethane sulfonate

25

 CF_3SO_3^-

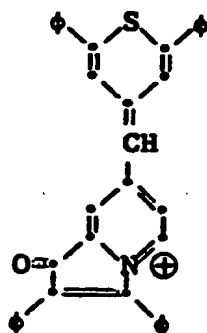
(780)

30

35

2,3-diphenyl-7-[(2,6-diphenyl-4-thio-
pyranylidene)methyl]-1-indolizininium
trifluoromethane sulfonate

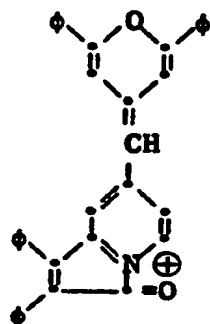
5

 CF_3SO_3^-

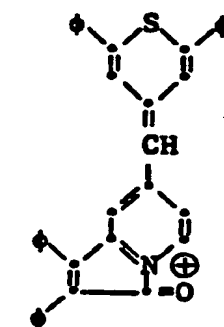
(730)

10

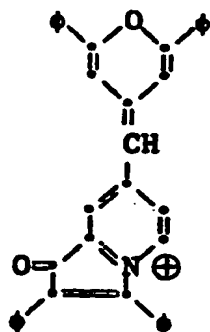
15

 BF_4^-
(640)

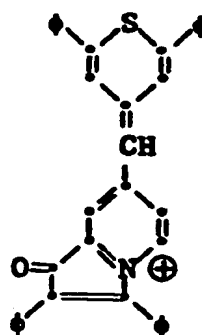
20

 ClO_4^-
(675)

25

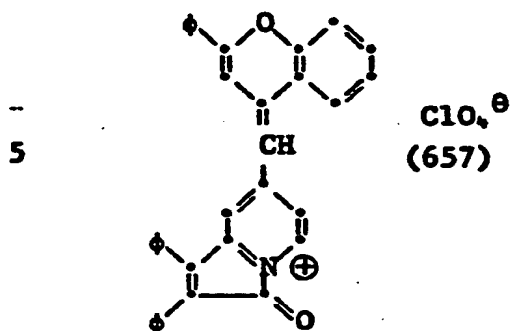
 BF_4^-
(690)

30

 ClO_4^-
(725)

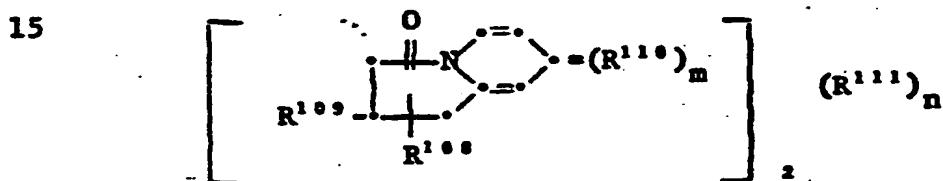
35

-86-



10 Another class of oxoindolizine dyes according to the invention is represented by the formula:

(XX)



20 wherein:

R^{100} and R^{101} are individually aryl containing 6 to 14 carbon atoms; or, alkyl containing 1 to 20 carbon atoms;

25 R^{110} is CH, phenylene or naphthylene;

R^{111} is phenylene or naphthylene; and

n and m are individually 0 or 1.

30 Examples of aryl groups which are suitable for use as R^{100} or R^{101} substituents include unsubstituted or substituted phenyl, naphthyl and anthryl.

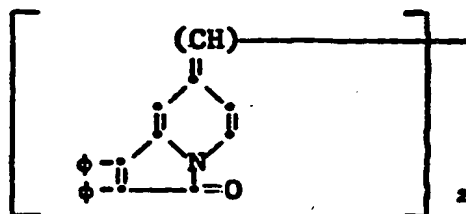
Examples of alkyl groups which are suitable for use as R^{100} or R^{101} substituents include methyl, ethyl, propyl, t-butyl, decyl, lauryl and eicosyl.

35 In oxoindolizine dyes according to the formula containing R^{110} and R^{101} , the oxoindolizine moiety represents a group completing an organic chromophore to produce the desired dye. Examples of such compounds are:

-87-

1,2-bis[7-(1,2-diphenyl-3(7H)-
indolizinyonylidene)]ethane

5

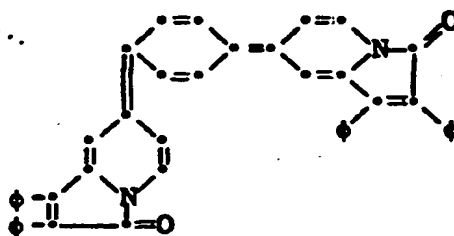


(685)

10

1,4-bis[7-(1,2-diphenyl-3(7H)-indoli-
zinyonylidene)]-2,5-cyclohexadiene

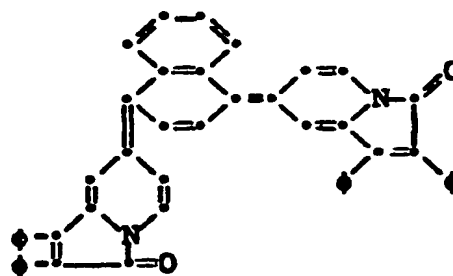
15



20

1,4-bis[7-(1,2-diphenyl-3(7H)-
indolizinyonylidene)]-2,3-benzo-2,5-
cyclohexadiene

25



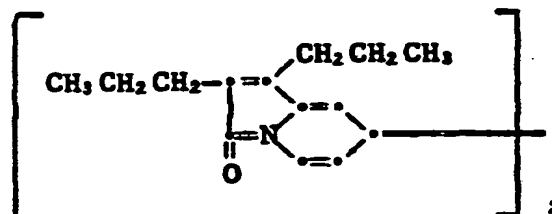
30

35

-88-

7,7'-bis[1,2-di-n-propyl-3(7H)-indolizonylidene]

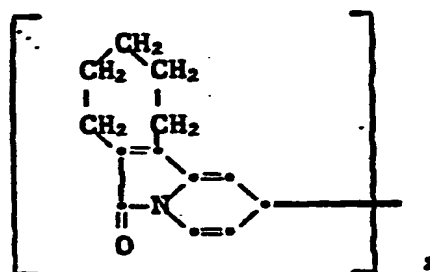
5



10

7,7'-bis-[1,2-pentamethylene-3(7H)-indolizonylidene]

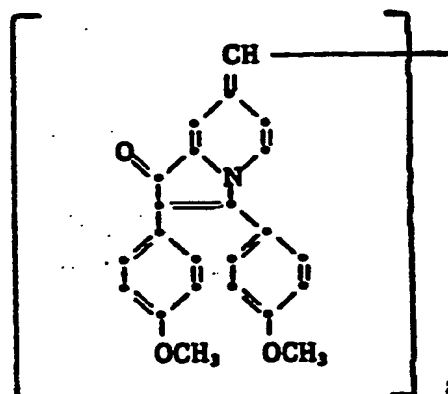
15



20

1,2-bis-[2,3-di-(4-methoxyphenyl)-1(7H)-indolizinonylidene]ethane

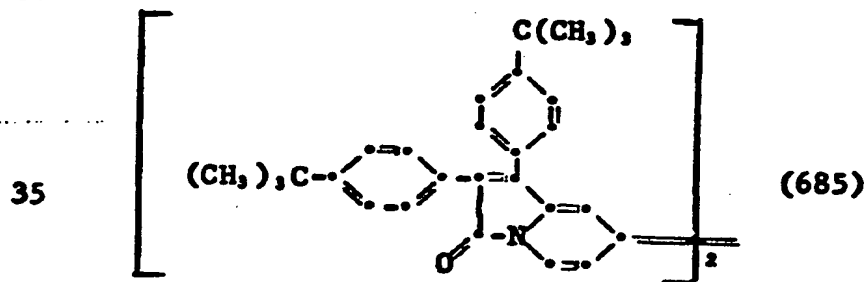
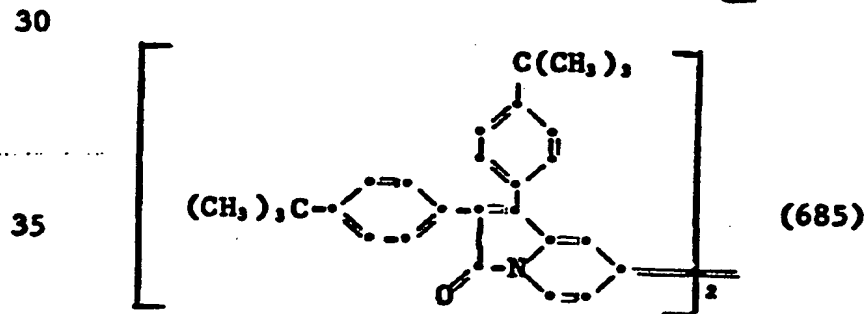
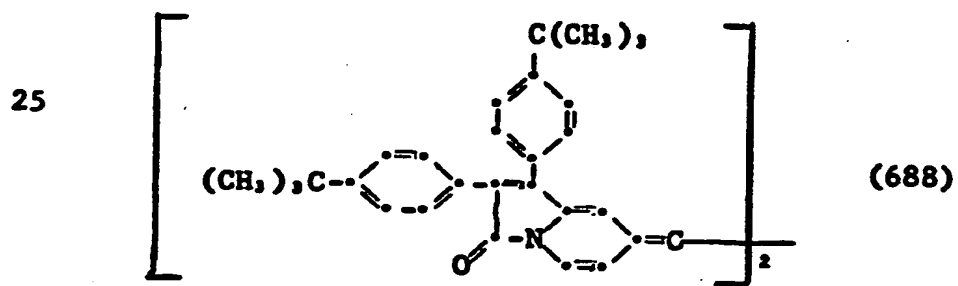
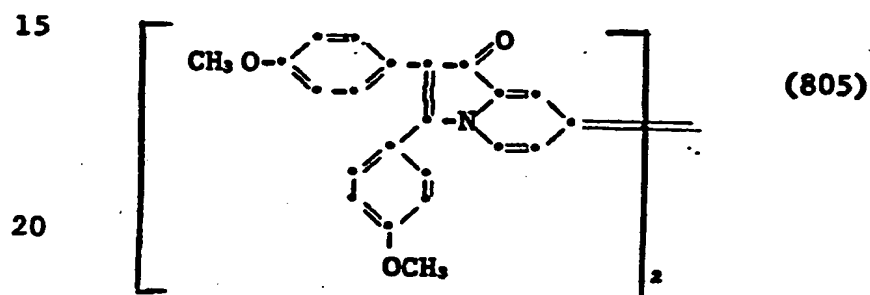
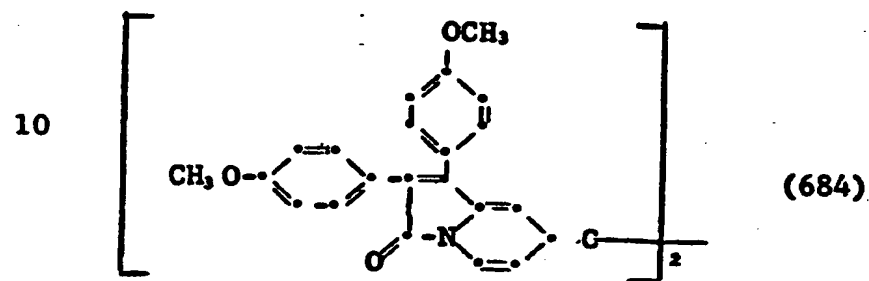
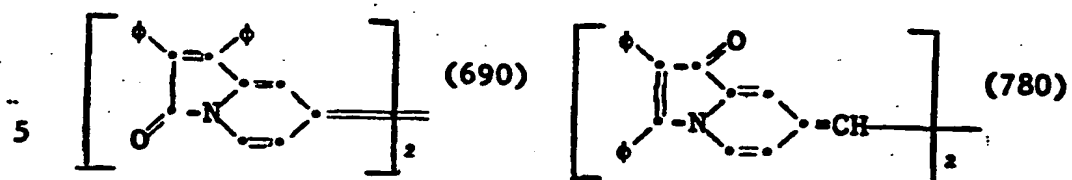
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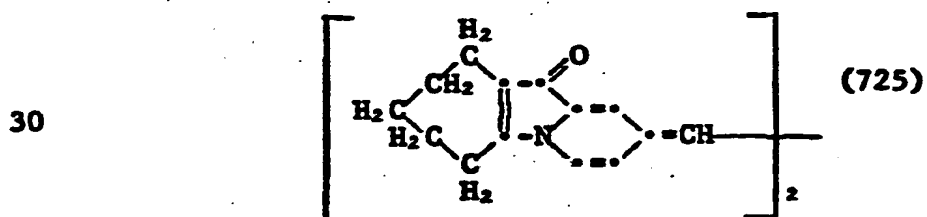
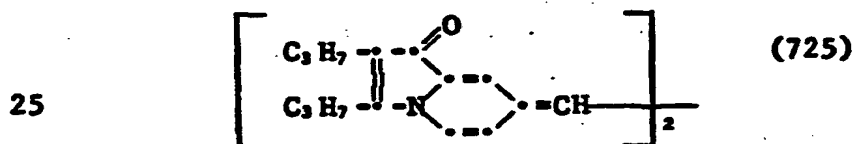
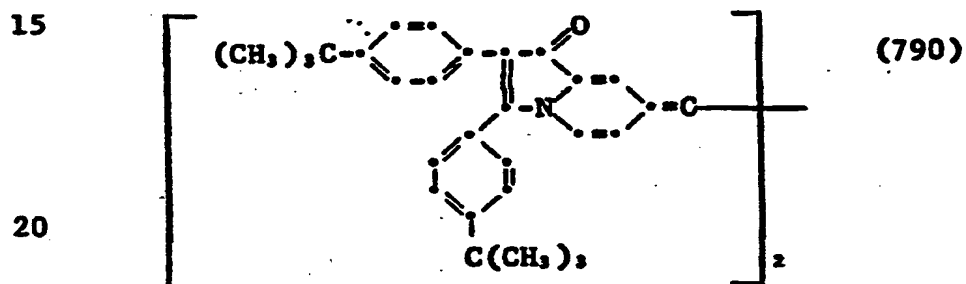
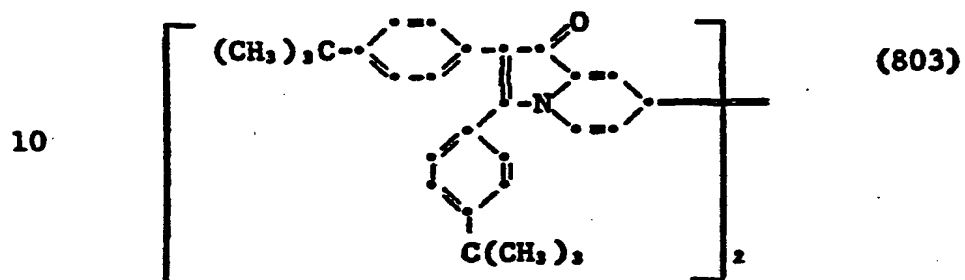
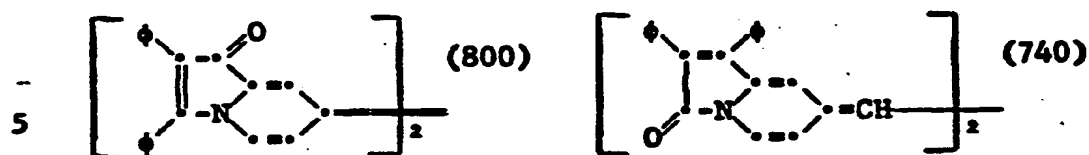


30

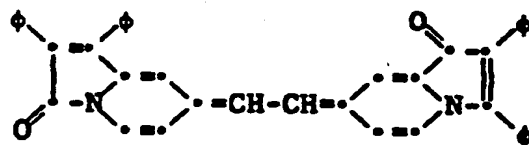
35

(790)

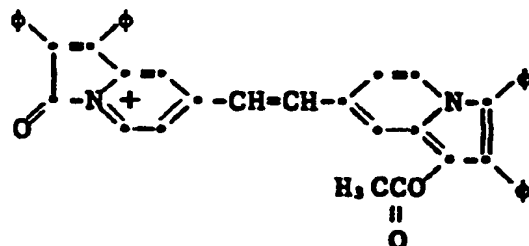




-91-



(740)

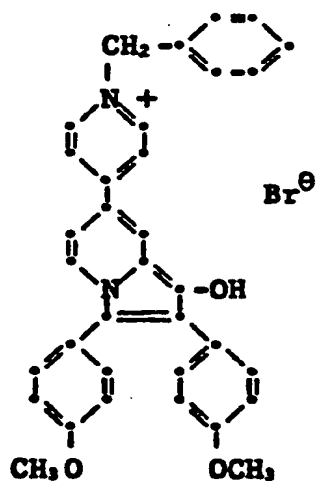


(840)

 BF_4^-

Examples of other dyes within the above structures (I) and (II) are as follows:

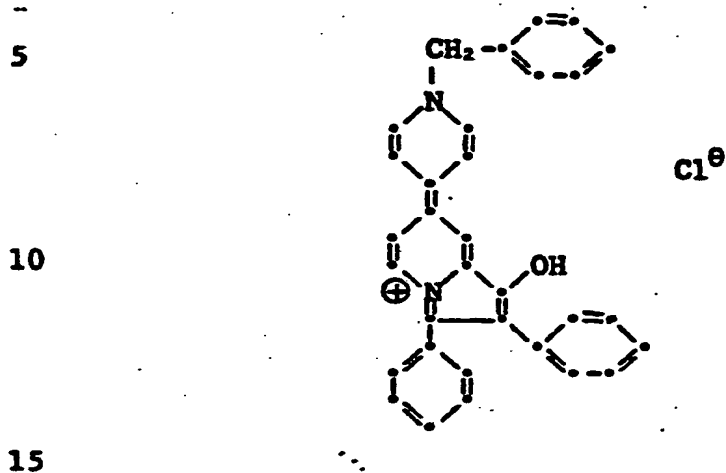
N-benzyl-4-{7-[2,3-di(4-methoxyphenyl)-3-indolizinolyl] pyridinium bromide



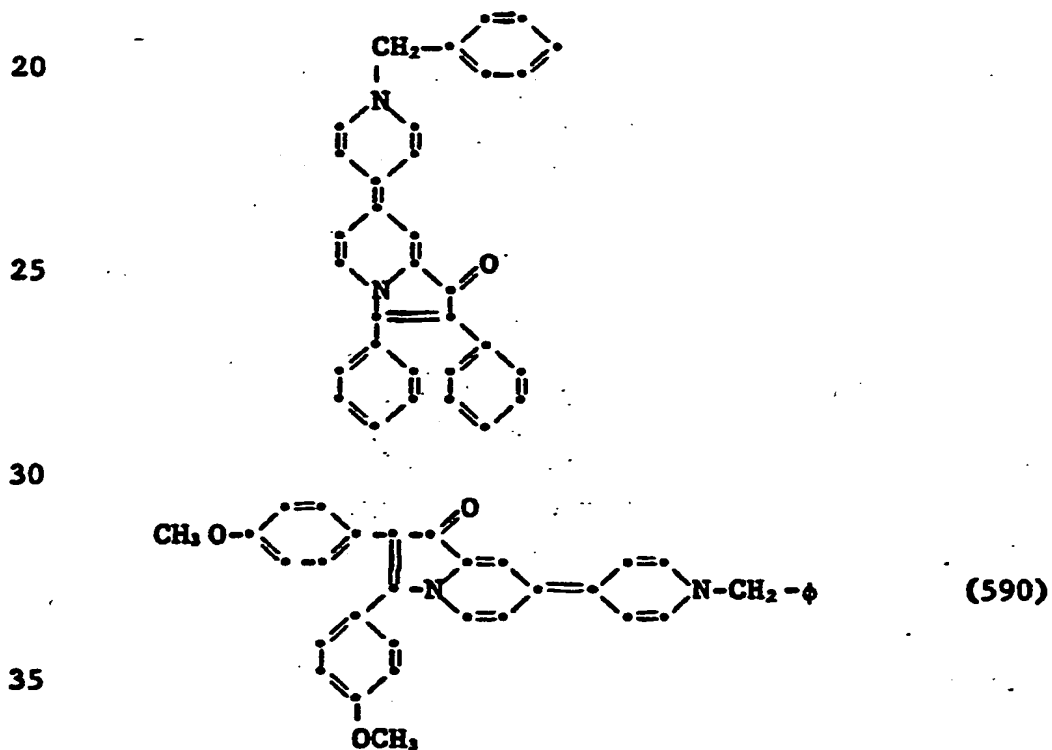
(590)

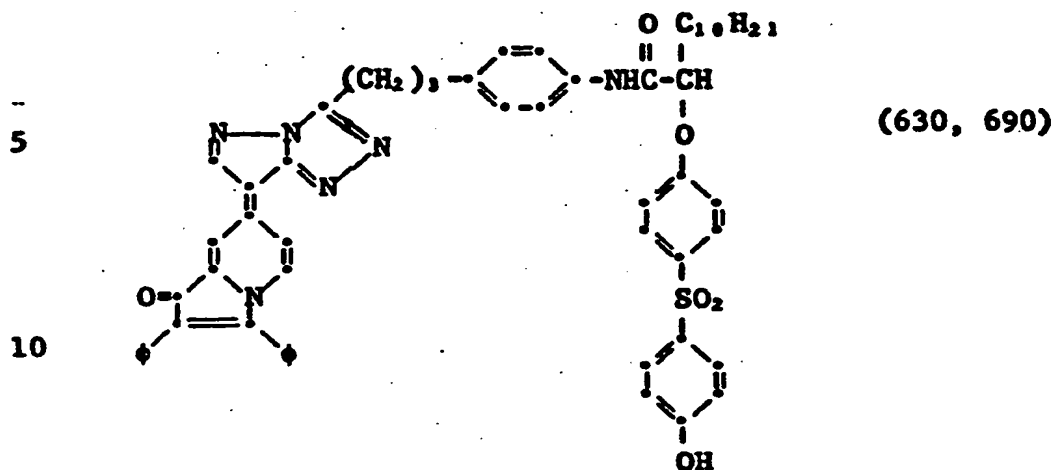
-92-

7-[4-(N-benzylpyridylidene)]-2,3-diphenyl-
1-hydroxy indolizinium chloride

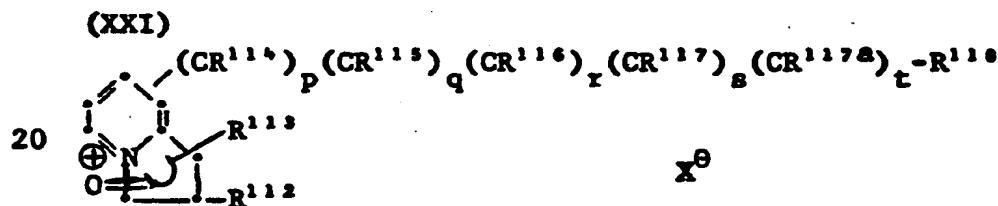


7-[4-(N-benzylpyridylidene)]-2,3-diphenyl-
1-indolizinone





15 Another class of dyes according to the invention is represented by the formula:



wherein

25 X^{\ominus} is an anion as defined above, preferably an acid anion such as methanesulfonate, trifluoromethanesulfonate, para-toluenesulfonate BF_4^{\ominus} bromide, chloride, iodide and sulfinate;

30 R^{112} and R^{113} are individually aryl containing 6 to 20 carbon atoms; aralkenyl containing 6 to 20 carbon atoms, and alkyl containing 1 to 20 carbon atoms; or R^{112} and R^{113} together represent the carbon atoms necessary to complete a 7- or

35 8-member cyclic structure;

-94-

R^{114} , R^{115} , R^{116} , R^{117} and R^{117a}
are individually hydrogen; alkyl containing
1 to 18 carbon atoms; phenyl; cyano;
carboxy; carboxamide; and carboalkoxy,
containing 2 to 18 carbon atoms; at least
one of R^{114} , R^{115} , R^{116} , R^{117} and R^{117a}
is hydrogen;

R^{118} is an electropositive or an
electronegative group necessary to complete
a chromophore, such as amino, anilino,
nitrophenyl, quino, pyranyl, pyridyl,
indoliziny, julolidyl and thiopyranyl;

p, q, r, s and t are individually 0 or 1;
any free bonds being satisfied by hydrogen
or unsaturated bonding as required.

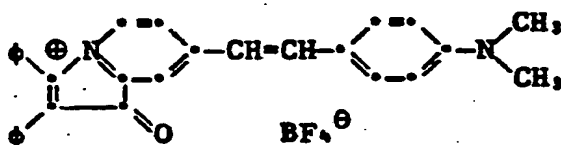
Aryl groups which are suitable for use as
 R^{112} and R^{113} substituents include unsubstituted
or substituted phenyl, naphthyl, anthryl,
methoxyphenyl and methoxynaphthyl.

Examples of aralkenyl groups which are
suitable for use as R^{112} and R^{113} substituents
include 2,2-diphenylvinyl, 2-phenylvinyl,
2-naphthylvinyl and 2-methyl-(2-phenylvinyl).

Alkyl groups which are suitable for use as
 R^{112} to and including R^{117a} include methyl,
ethyl, propyl, t-butyl, decyl and lauryl.

Examples of compounds within this class are
as follows:

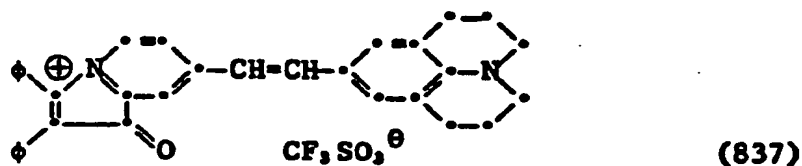
7-[2-(4-N,N-dimethylaminophenyl-1-ethenyl)-
2,3-diphenyl-1-indolizinium] fluoroborate



(780)

2,3-diphenyl-7-[2-(9-julolidyl)-1-ethenyl]
1-indolizininium trifluoromethane sulfonate

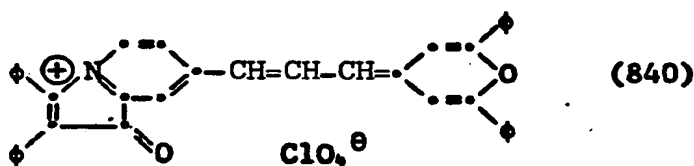
5



10

2,3-diphenyl-7-[3-(2,3-diphenyl-4(4H)-
pyranylidene-1-propenyl)-1-
indolizininium perchlorate

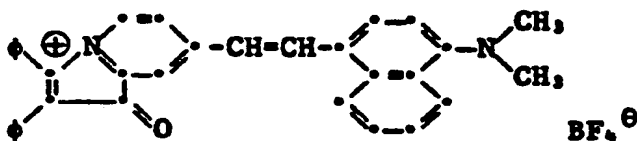
15



20

7-[2-(4-N,N-dimethylaminonaphthyl)-1-
ethenyl]-2,3-diphenyl-1-
indolizininium fluoroborate

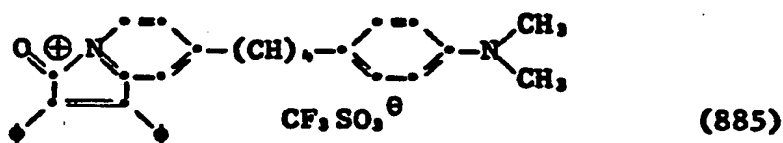
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30

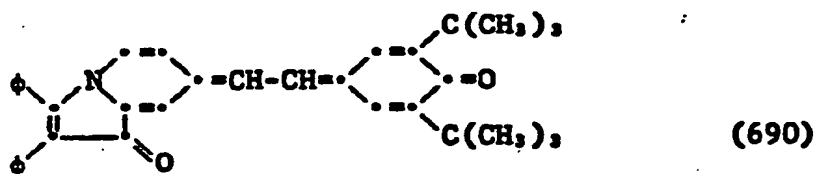
7-[4-(4-dimethylaminophenyl)-1-butadienyl]-
1,2-diphenyl-3-indolizininium trifluoro-
methane sulfonate

35



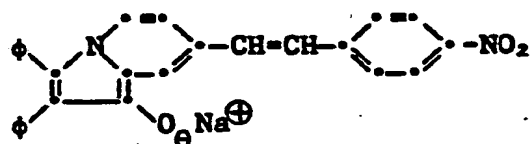
1-(3,5-di-tert-butyl-4-oxo-1-phenylidene)-
2-[7-(2,3-diphenyl-1-(7H)-indolizinon-
ylidene)]ethane

5



10

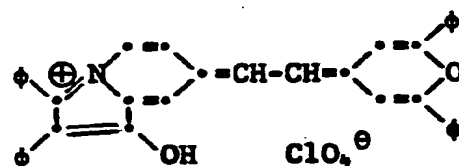
2,3-diphenyl-7-[2-(4-nitrophenyl)-1-
ethenyl]-1-indolizinol sodium salt



15

2,3-diphenyl-7-[2-(2,6-diphenyl-4-(4H)-
pyranylidene)-1-ethylidene]-1-hydroxy-
(7H)-indolizinium perchlorate

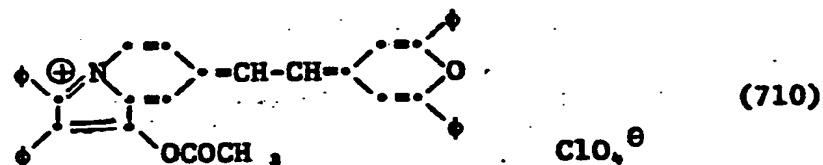
20



25

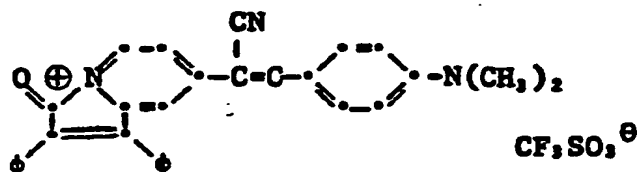
2,3-diphenyl-7-[2-(2,6-diphenyl-4-(4H)-
pyranylidene)-1-ethylidene]-1-acetoxy-(7H)-
indolizinium perchlorate

30

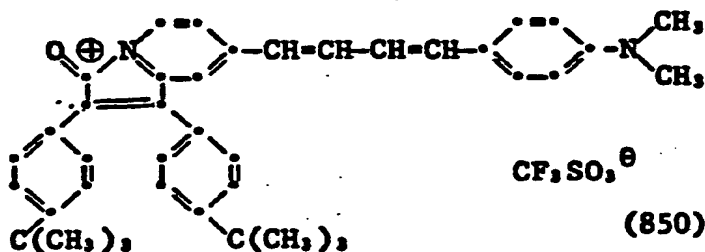


35

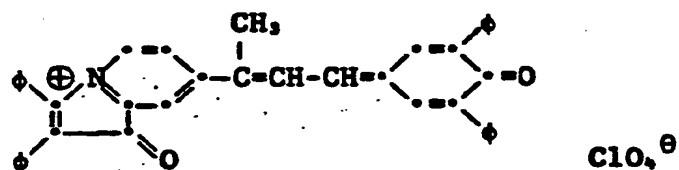
7-[1-cyano-2-(4-dimethylaminophenyl)-1-ethenyl]-1,2-diphenyl-3-indolizininium trifluoromethane sulfonate



1,2-di-tert-butylphenyl-7-[4-(4-dimethylaminophenyl)-1-(1,3-butadienyl)]-3-indolizininium trifluoromethane sulfonate

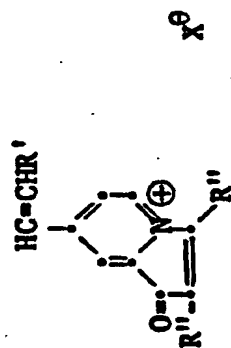


2,3-diphenyl-7-4-(2,6-diphenyl-4(4H)-pyranylidene)-2-(2-butenyl)-1-indolizininium trifluoromethane sulfonate



30 Additional compounds of this class are shown below in Tables I and II:

TABLE I



Compound	R'	R''	X ^θ	λ _{max} (nm)
1-1			BF ₃	780
1-2			BF ₃	780
1-3			BF ₃	837

TABLE I (Cont'd.)

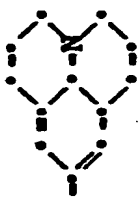

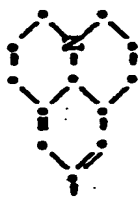



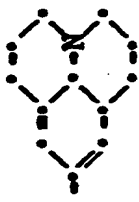

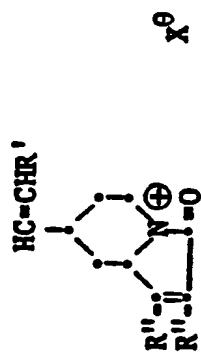
Compound	R'	R''	X ^θ	λ _{max} (nm)
1-4			BF ₃	838
1-5			CF ₃ SO ₃	838
1-6			BF ₃	840
1-7			CF ₃ SO ₃	840

TABLE II



Compound	R'	R''	X ^θ	λ _{max} (nm)
2-1			BF ₄	788
2-2		$-\text{t-C}_6\text{H}_5-$	BF ₄	790
2-3			CF ₃ SO ₃	788
2-4		$-\text{t-C}_6\text{H}_5-$	CF ₃ SO ₃	790

-102-

A further class of dyes according to the invention is represented by the structural formula:

(XXII)



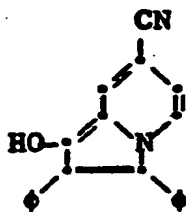
10 wherein:

R^{119} and R^{120} are individually aryl containing 6 to 20 carbon atoms, such as phenyl and naphthyl; or, alkyl containing 1 to 18 carbon atoms, such as methyl, ethyl, propyl, decyl and lauryl;

R^{121} is cyano, carboxy, formyl, acyl containing 2 to 18 carbon atoms, such as acetyl, propionyl and lauroyl; carboalkoxy containing 2 to 18 carbon atoms, such as carbomethoxy, carboethoxy and carbobutoxy; or aminocarbonyl containing 1 to 18 carbon atoms, such as unsubstituted aminocarbonyl, methylaminocarbonyl and dimethylamino-carbonyl which enables the compound to be a dye.

The compounds in this class are shown in the enol form, rather than the keto form. Examples of compounds within this class are as follows:

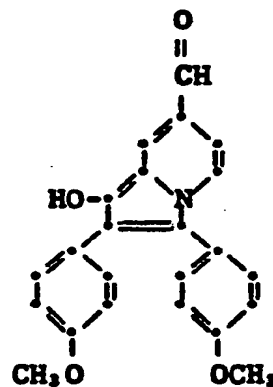
30 7-cyano-2,3-diphenyl-1-indolizinol



(405)

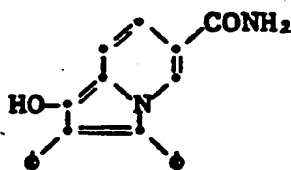
-103-

7-formyl-2,3-di-(4-methoxyphenyl)-1-indolizinol

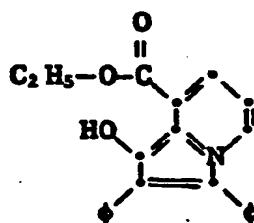


(423)

6-aminocarbonyl-2,3-diphenyl-1-indolizinol

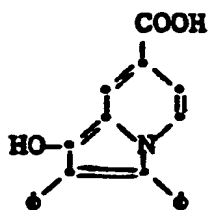


8-carboethoxy-2,3-diphenyl-1-indolizinol



(490)

7-carboxy-2,3-diphenyl-1-indolizinol



(420)

5
10 The oxoindolizine dyes according to the invention are prepared by a method comprising reacting (A) a suitable pyridine compound with (B) a cyclopropenone compound, generally a photosensitive cyclopropenone. The resulting oxoindolizine or
15 oxoindolizine compound is a new dye or a new dye is produced from the resulting oxoindolizine or oxoindolizinium compound by reacting the product with an appropriate color-forming compound, such as a color-forming coupler. Such a method is illustrated
20 by the preparation of dyes represented by formulas I and II above comprising the steps:

- (1) reacting (A) a pyridine compound with (B) a cyclopropenone compound and optionally
- (2) reacting the resulting product from (1) with a color-forming compound, such as a
25 color-forming coupler, preferably in the presence of an oxidizing or dehydrating agent that catalyzes formation of a dye. Some of the compounds produced in step (1) are dyes which absorb in the visible region
30 of the electromagnetic spectrum.

Optimum methods for preparation of dyes according to the invention will vary, depending upon the desired dye, the starting material, the cyclopropenone, the color-forming coupler, the
35 pyridine compound, solvents present, reaction

-105-

temperature, concentration of reactants and catalyst present. The cyclopropanone and pyridine compounds are mixed in about stoichiometric concentrations. However, it is often useful to mix the reactants with an excess of the pyridine compound to provide better yields or different isomers.

The reactants for forming a dye according to the invention can be mixed in a suitable reaction medium. For example, the cyclopropanone and pyridine compounds are mixed in an appropriate reaction medium, such as an organic solvent or medium that forms a suitable composition, for subsequent utilization of the dye which is formed.

A reaction medium which comprises a solvent for the reactants is most useful. A useful solvent includes, for example, pyridine, chlorinated hydrocarbons, such as methylene chloride and chlorobenzene, toluene, dioxane, and tetrahydrofuran. Pyridine and some pyridine related solvents, such as 4-picoline, are especially useful in producing isomers. The reactants are mixed at room temperature (about 19°C) and then heated to within the range of about 50 to about 150°C. The optimum reaction temperature will be influenced by the choice of solvent, the particular reactants, the desired dye, and other described factors.

When a dye according to the invention is formed by the reaction of a cyclopropanone with a pyridine compound and suitable color-forming compound, such as a color-forming coupler, it is preferred that the reaction be carried out in chemical association with an appropriate oxidant, such as elemental iodine, oxygen, copper bromide, copper chloride, copper acetate, benzoyl peroxide or copper acetylacetonate. The concentration of oxidant will vary, depending upon the particular reactants,

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processing conditions, desired dye, and reaction medium. An oxidant is especially useful in the reaction of a cyclopropanone with a pyridine compound and an active methylene coupler.

5 In preparing an oxoindolizine dye by the reaction of pyridine compound with a cyclopropanone compound, the condensation is generally carried out in a solvent. The concentration of reactants is generally about stoichiometric. However, an excess
10 of pyridine or picoline is often useful. The reaction temperature is generally within the range of 0°C to 95°C. The reaction is preferably carried out in chemical association with an oxidant, such as copper ions or air.

15 An especially useful method according to the invention comprises preparation of a dye represented by the structure (XXI) comprising reacting a compound represented by the structure

20 (XII)



25

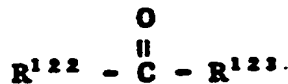
wherein

X^6 , R^{50} , R^{51} and R^{52} are as defined above,

with an aldehyde or ketone represented by the formula

30

(XXIV)



35

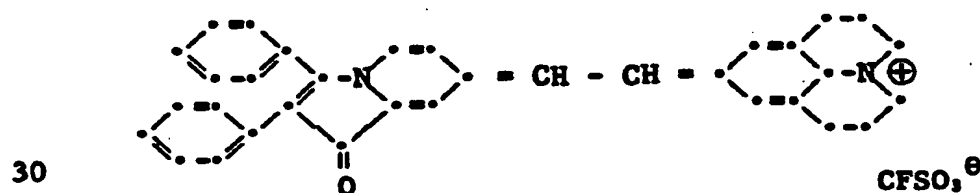
wherein

-107-

5 R^{122} and R^{123} are individually hydrogen or substituents that do not adversely affect the oxoindolizinium dye, such as alkyl containing 1 to 20 carbon atoms, for example, methyl, ethyl, propyl, butyl, decyl and lauryl; aryl containing 6 to 20 carbon atoms, such as phenyl, tolyl, and naphthyl; or a heterocyclic group, such as pyridyl and julolidyl; and at least one of R^{122} and R^{123} is a monovalent group

10 which completes a chromophore as defined. Such compounds include, for example, pyrylium, flavylum, dimethylamino benzaldehyde and cinnamaldehyde compounds. These reactants (XII) and (XXIV)
 15 are reacted in about equimolar proportions in a suitable solvent, such as acetic anhydride, with or without a catalyst, such as piperidine or sodium acetate, at a temperature within the range of about 20°C to about 140°C. The resulting dye crystallizes
 20 from the medium or is precipitated by addition of a non-solvent, such as water, ethyl ether or cyclohexane. An example of such a method according to the invention is a method of preparing a dye represented by the formula:

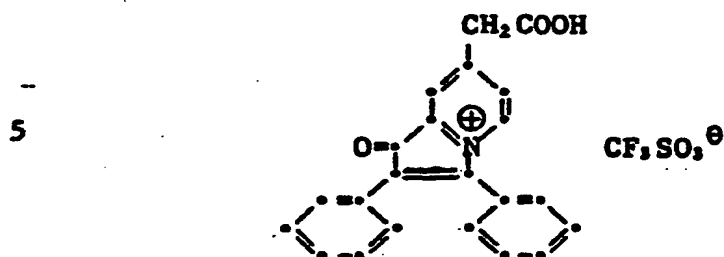
25



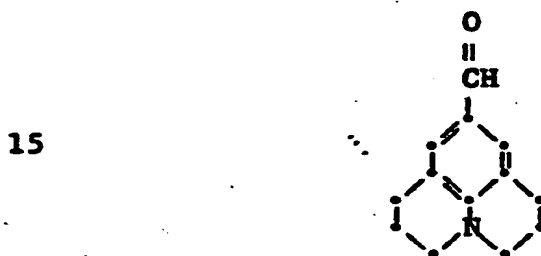
comprising the step:

(1) reacting a compound represented by the formula:

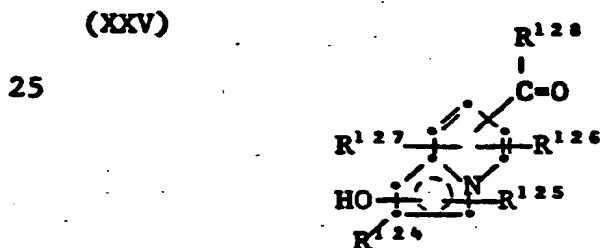
35



10 with a compound represented by the formula:



20 Another method of preparing dyes according to the invention comprises reacting an indolizinol represented by the formula:



30 wherein

R¹²⁴ and R¹²⁵ are individually aryl containing 6 to 14 carbon atoms, such as phenyl, xyl, methoxyphenyl and naphthyl; or, alkyl containing 1 to 20 carbon atoms, such as methyl, ethyl, propyl, decyl and lauryl;

35

5 R^{126} is hydrogen, cyano, carboxy, formyl, acyl containing 2 to 18 carbon atoms, such as acetyl, propionyl, and lauroyl; carboalkoxy containing 2 to 10 carbon atoms, such as carbo-methoxy, carboethoxy and carbobutoxy; or amino-carbonyl containing 1 to 18 carbon atoms, such as unsubstituted aminocarbonyl, methylamino-carbonyl and dimethylaminocarbonyl; and alkyl containing 1 to 18 carbon atoms, such as methyl, 10 ethoxy, propyl, butyl, decyl and lauryl;

R^{127} is hydrogen or alkyl containing 1 to 4 carbon atoms, such as methyl, ethyl, propyl and butyl;

15 R^{128} is alkyl containing 1 to 18 carbon atoms, such as methyl, ethyl, propyl, butyl, decyl and lauryl; or aryl containing 6 to 14 carbon atoms, such as phenyl, tolyl, xylyl and naphthyl;

20 with an active methylene coupler, such as represented by formula (IX). The indolizinol represented by formula (XXV) and the active methylene coupler are reacted in about equimolar proportions in a suitable solvent, such as acetic anhydride, preferably with a catalyst, such as piperidine or 25 sodium acetate, at a temperature within the range of 20°C to 140°C. The resulting dye crystallizes from the reaction medium and is preferably precipitated by the addition of a non-solvent, such as water, ethyl ether or cyclohexane.

30 Many oxoindolizine and oxoindolizinium dyes within Structures I and II are useful in imaging, such as in photothermographic imaging or in laser recording and reading applications. Especially useful dyes according to the invention are compounds 35 that are image dyes or, alternatively, are capable of forming image dyes. Selection of an optimum

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indolizininone or indolizinium dye will depend upon such factors as the desired use, processing conditions, desired image, particular components with the dye, exposure means to form an image, and stability of the dye.

The following examples are included for a further understanding of the invention.

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-111-

Example 1 -- Preparation of 7,7'-(1,2-ethane-(E)-diylidene)bis-1,2-di-(4-tert-butylphenyl)-3(7H)-indolizinone

A solution (10 percent by weight) of
5 2,3-di(4-tertiarybutylphenyl) cyclopropenone, in
4-picoline (pyridine compound), was prepared
containing a trace of cupric acetate (catalyst).
The solution was sparged with a stream of air to
provide agitation and excess oxygen. The solution
10 was heated on a steam bath to 80°C to 95°C for 15
minutes. A pasty cyan-colored slurry resulted. The
resulting mixture was filtered to remove excess
picoline, and the colored solids washed with
acetone. The solids were dried under vacuum to
15 remove the acetone-washed solvent. A 25 percent
yield of the desired dye was obtained based on the
cyclopropenone starting material. The dye had a
maximum absorption at 695 nm in chloroform solu-
tion. The structure was confirmed by mass spectro-
20 scopy, nuclear magnetic resonance, infrared spectral
analysis and x-ray diffraction.

Example 2 -- Preparation of 7-(4-Pyridyl)-2,3-
di-(4-methoxyphenyl)indolizinol,
Benzyl Bromide Salt

25 Equimolar amounts of benzyl bromide and
4,4'-di-pyridine were dissolved in N,N-dimethyl-
formamide to form approximately a 10 percent by
weight solution. The solution was heated for 10
minutes on a steam bath at 95°C to form the quater-
30 nary salt of bipyridine. The reaction mixture was
cooled slightly, and an equimolar amount of 2,3-di-
(4-methoxyphenyl) cyclopropenone was added to the
solution. The reaction mixture was heated for 15
minutes and quenched in excess cold water. A solu-
35 tion of 48 percent hydrobromic acid was added to the

-112-

water-N,N-dimethylformamide solution to precipitate the desired dye product. The precipitated dye was removed by filtration and dried under vacuum. The dye had a maximum absorption density at 535 nm in chloroform solution. The desired dye structure was confirmed by mass spectroscopy, nuclear magnetic resonance and infrared spectral analysis.

Example 3 -- Preparation of 7-Dibenzoylmethylidene-2,3-di(4-methoxyphenyl)-1(7H)-indolizinone

A 10 percent solution of 2,3-di(4-methoxyphenyl) cyclopropenone in pyridine was refluxed under nitrogen for 15 minutes. The resulting solution was cooled slightly, and an equivalent amount of dibenzoylmethane based on the cyclopropenone was added to the green solution. The reaction mixture was refluxed for 60 minutes. The resulting reaction mixture was again cooled, and four equivalents of iodine dissolved in a small amount of pyridine was added to the reaction mixture. The mixture was further heated at 90°C on a steam bath for 15 minutes. The bright blue solution was quenched by pouring it into cold excess dilute hydrochloric acid. The desired dye precipitated and was removed from the solution by filtering. A 95 percent yield of the desired dye was obtained based on the starting cyclopropenone. The dye was chromatographed on silica gel to provide a purified product. The maximum absorption of the dye was at 605 nm in chloroform solution. The structure of the dye was confirmed by mass spectroscopy, nuclear magnetic resonance and infrared analysis.

Example 4 -- Preparation of 7-Formyl-2,3-di(4-methoxyphenyl)-1-indolizinol

Equivalent amounts of 4-formylpyridine and 2,3-di(4-methoxyphenyl) cyclopropenone were

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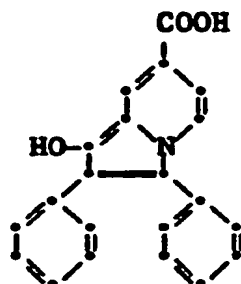
dissolved in sufficient para-dioxane to form approximately a 10 percent solution. The mixture was refluxed at 102°C under nitrogen for 2 hours. Sufficient water was then added to the reaction mixture to bring it to the cloud point at 80°C. The reaction mixture was then cooled to room temperature, and the product allowed to crystallize. The crystals were collected by filtration, and washed with a small amount of water. The dried crystals were the desired dye. The dye was produced in a 95 percent yield based on the amount of cyclopropanone. The yellow dye had a maximum absorption of 435 nm in chloroform solution. The structure of the dye was confirmed by mass spectroscopy, nuclear magnetic resonance and infrared analysis.

Examples 5-8 --

Other yellow dyes were prepared by a modification of the procedure described in Example 4. The modification consisted of substituting the particular pyridine needed to obtain the desired dye for the 4-formyl pyridine described in Example 4. Structures were confirmed by mass spectrometry, nuclear magnetic resonance and elemental analysis. Examples of the yellow dyes prepared are as follows:

Example 5:

7-carboxyl-2,3-diphenyl-1-indolizinol



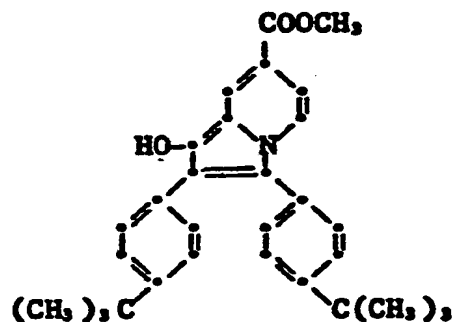
λ_{\max} 430

Example 6:

7-carbomethoxy-2,3-di(4-tert-butylphenyl)-
1-indolizinol

5

10

 λ_{\max} 425

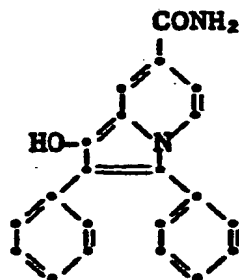
15

Example 7:

7-aminocarbonyl-2,3-diphenyl-1-indolizinol

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25

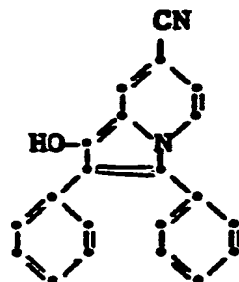
 λ_{\max} 405

Example 8:

7-cyano-2,3-diphenyl-1-indolizinol

30

35

 λ_{\max} 410

-115-

Example 9 -- Preparation of 1,2-di-(4-tert-butylphenyl)-7-[4-(4-dimethylaminophenyl)-1-(1,3-butadienyl)]-3-indolizininonium trifluoromethanesulfonate

5 Equivalent amounts of 4-dimethylamino-cinnamaldehyde and 1,2-di(tert-butylphenyl-7-methyl-3-indolizininonyl trifluoromethane sulfonate were dissolved in acetic anhydride to form approximately a 10 percent solution. The reaction mixture
10 was heated at 70-90°C for five minutes, cooled to room temperature and diluted with diethyl ether and the resulting product collected by filtration. The crude product was recrystallized from acetone to furnish the desired dye.

15 Example 10 -- Preparation of 7-(4-dimethyl-amino-phenyl)-2,3-diphenyl-1-indolizininonium fluoborate

 A 10% solution of 1,2-diphenyl-1-indolizininonium triiodide in dimethylaniline was warmed at
20 70-90°C for 10 minutes. The resulting solution was cooled and diluted with diethyl ether and the resulting solid redissolved in acetone. The desired dye was precipitated by the addition of dilute fluoboric acid to the solution.

25 Example 11 -- Preparation of 7-diethylamino-2,3-diphenyl-1-indolizininonium fluoborate

 A 10% solution of 2,3-diphenyl-1-indolizininonium triiodide in pyridine was treated with two equivalents of anhydrous diethyl amine and heated at
30 70-90°C for 15 minutes. The reaction mixture was cooled and poured into diethyl ether and filtered to furnish the crude dye. The dye was washed thoroughly with water to remove soluble salts to furnish purified product.

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Examples 12-14 -- Use of Dyes in Optical Disc for
Laser Writing and Reading

Oxoindolizine and oxoindolizinium dyes for use in an optical disc were selected to provide the desired characteristics for laser writing and reading including among other characteristics, the desired solubility, absorption and stability characteristics.

In each of the examples an optical disc for laser writing and reading was prepared by coating, on a support designed for an optical disc, a layer of an amorphous composition comprising a binder, such as cellulose nitrate, and an oxoindolizine or oxoindolizinium dye having an absorption at a wavelength at which the laser was tuned, such as a wavelength in the range of about 300 to about 1000 nanometers. Optical discs were prepared by techniques described in, for example, "Disc-Storage Technology" by Robert M. White, Scientific American, August 1980, beginning at page 138, and Research Disclosure, November, 1978, Item No. 17522, the descriptions of which are incorporated herein by reference.

The dyes of Examples 12, 13 and 14 were individually incorporated in a coating composition containing cellulose nitrate (binder) and cyclohexanone (solvent). The resulting compositions were coated on optical disc supports containing a reflective metal layer, such as aluminum. The resulting optical discs were imagewise exposed to a laser emitting at 800 nanometers pulsed at 10 MHz and a 50% duty cycle in a 30 KHz bandwidth to provide an image on each optical disc. Reading from the exposed optical discs was by monitoring the feedback from the same laser. The following dyes were tested in the video discs:

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<u>Example No.</u>	<u>Dye</u>
12	2,3-diphenyl-7-[2-(9-julolidinyl)ethenyl]-1-oxo-1H-indolizinium trifluoromethanesulfonate
13	2,3-bis(4-t-butylphenyl)-7-[2-(9-julolidinyl)-ethenyl]-1-oxo-1H-indolizinium trifluoromethanesulfonate
14	1,2-bis (4-t-butylphenyl)-7-[2-(9-julolidinyl)-ethenyl]-3-oxo-3H-indolizinium trifluoromethanesulfonate

15 An image was recorded and read on each of the optical discs. The recording power at the discs was 12 mW in each case.

Example 15 -- Production of a Red Dye in a Coating

20 A solution was prepared containing 525 mg of poly(ethylene-co-1,4-cyclohexylenedimethylene-1-methyl-2,4-benzenedisulfonamide) (binder), 400 mg of 1-methyl-4-(4-pyridyl)pyridinium-para-toluene-sulfonate (pyridine compound) and 9.980 g of 2-methoxyethanol (solvent). The

25 polysulfonamide binder and quaternary salt (pyridine compound) were dissolved in the 2-methoxyethanol by gentle agitation at room temperature (19°C). A clear lacquer solution resulted which was coated on a poly(ethylene terephthalate) film support at a wet

30 coating thickness of 0.125 mm. The coating was dried by heating the material to about 24°C for 30 minutes in a stream of air.

A second solution was prepared by dissolving 525 g of poly(styrene-co-butadiene) (KRO-3, which is a

35 trade name of and available from Phillips Petroleum

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Company, U.S.A.), in 9.98 g of toluene with 40 mg of 1-phenyl-2-(para-methoxy-phenyl)cyclopropanone (photosensitive cyclopropanone compound). Solution was produced by stirring at 22°C for several hours.

- 5 A clear lacquer solution resulted which was coated directly over the first layer containing the pyridine compound. A wet coating thickness of 0.125 mm was applied. The resulting composite two-layer element was dried by warming to 45°C for 10 30 minutes. The resulting element was exposed to a 250 watt mercury lamp for 20 seconds at a distance of 7.6 cm. The desired dye was produced by heating the element, after exposure, to 150°C for 3 seconds on a heated aluminum block. A brilliant red dye was 15 formed which had a maximum absorption at 535 nm.

Example 16 -- Production of a Blue Dye in a Coating

- A coating solution was prepared by dissolving 0.500 g of the polysulfonamide binder as described in Example 15 and 500 mg of 4-azastyryl- 20 1-methyl-pyridinium para-toluenesulfonate (pyridine compound) in 10 g of 2-methoxyethanol (solvent). Solution was produced by stirring at room temperature (19°C). A clear lacquer solution resulted which was coated on a poly(ethylene terephthalate) 25 film support by means of a doctor blade to produce a wet coating thickness of 0.125 mm. The resulting coating was dried by heating the coating to about 24°C for 30 minutes in a stream of air.

- A second solution was prepared by dissolving 30 25 mg of phenylanisyl cyclopropanone and 0.50 g of poly(styrene-co-butadiene) resin in 10.0 g of toluene. A clear solution which resulted upon stirring the mixture for 3 hours at room temperature (19°C) was coated directly over the first layer 35 containing the pyridine compound. A wet coating

-119-

thickness of 0.125 mm was applied by means of a doctor blade. The composite two-layer element was dried by warming the resulting coating to about 24°C for 30 minutes in a stream of air. A brilliant clear transparent film was obtained.

The resulting element was imagewise exposed and then heated as described in Example 15. A blue dye was formed which had a maximum absorption at 575 nm.

10 Example 17 -- Production of a Green Dye in a Coating

A coating solution was prepared by dissolving 0.50 g of poly(styrene-co-butadiene) resin and 125 mg of 4,4'-dipyridylethylene (pyridine compound) in 10.0 g of toluene (solvent). A clear solution which resulted upon stirring at room temperature (19°C) was coated on a poly(ethylene terephthalate) film support containing a gelatin subbing layer at a wet coating thickness of 0.125 mm. The resulting coating was dried by heating to 24°C for 30 minutes. A second layer was coated over the layer containing the pyridine compound. This second layer was prepared from a coating solution produced by dissolving 0.50 g of poly(vinyl alcohol) in 9.50 g of water. The composition containing the poly(vinyl alcohol) was coated at a wet coating thickness of 0.125 mm over the first layer. The resulting composite film was dried by heating to 24°C for 30 minutes. A top layer was prepared by coating a solution containing 125 mg of photosensitive phenylanisyl cyclopropanone and 0.50 g of poly(styrene-co-butadiene) dissolved in 10.0 g of toluene. The top layer was coated at a wet coating thickness of 0.125 mm. The resulting composite film was dried for 30 minutes at 24°C in an air stream. The composite film was imagewise exposed for 40

-120-

seconds and then heated as described in Example 15. A dye was produced which had a maximum absorption in the infrared region of the electromagnetic spectrum at 815 nm.

5 Example 18 -- One Layer Element

A coating solution was prepared by dissolving .50 g of poly(styrene-co-butadiene) resin, 40 mg of o,p-dianisylcyclopropanone (photosensitive cyclopropanone), and 40 mg of 1,2-bis(4-pyridyl)-ethylene (pyridine compound) in 10.0 g of toluene. The solution was coated on a poly(ethylene terephthalate) film support at a wet coating thickness of 0.125 mm. The coating was dried by standing at 24°C for two hours. The resulting
15 element was exposed to a 250 watt mercury lamp for 20 seconds at a distance of 7.6 cm through a mask to produce a developable image in the photographic element. The desired dye was produced by heating the element, after exposure, to 150°C for 10 seconds
20 on a heated aluminum block. An infrared dye was formed in the film with a maximum absorption at 830 nm.

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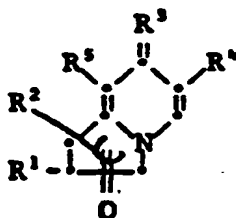
CLAIMS:

1. A method of preparing an oxoindolizine or an oxoindolizinium dye compound including the steps of:

- 5 1) reacting (A) a pyridine compound having hydrogen atoms on the carbon atoms ortho to the heterocyclic nitrogen atom, with (B) a cyclopropenone compound; and optionally
- 10 2) reacting the resulting product from (1) with a color-forming compound preferably in the presence of an oxidant that catalyzes the formation of said dye compound .

2. A method according to Claim 1 characterized in that said dye compound has the

15 formula:



wherein:

20 R¹ and R² are individually alkyl containing 1 to 18 carbon atoms; aryl containing 6 to 20 carbon atoms; or polystyryl having appended indolizine or indolizinium groups or combinations thereof;

25 R³ is a divalent group which, with the indolizinone nucleus, completes an organic chromophore;

30 R⁴ is hydrogen; alkyl containing 1 to 18 carbon atoms; cyano; acyl containing 2 to 20 carbon atoms; carboalkoxy containing 2 to 18 carbon atoms; aminocarbonyl containing from 1 to 18 carbon atoms;

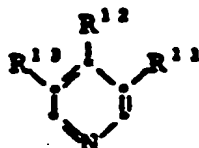
-122-

acyloxy containing 2 to 18 carbon atoms;
bromine or chlorine; and

R^8 is hydrogen; chlorine; bromine or
alkyl containing 1 to 18 carbon atoms;

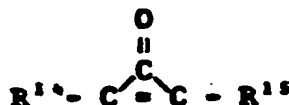
5 which dye compound is prepared by

1) reacting (A) a pyridine compound having the
formula:



10

with (B) a cyclopropenone compound
represented by the formula:



15

wherein

20

R^{11} is hydrogen; alkyl containing 1 to 18
carbon atoms; cyano; acyl containing 2 to
20 carbon atoms; carboalkoxy containing 2
to 18 carbon atoms; aminocarbonyl
containing 1 to 18 carbon atoms; acyloxy
containing 2 to 18 carbon atoms; bromine or
chlorine;

25

R^{12} is hydrogen; alkyl containing 1 to
18 carbon atoms; cyano; acyl containing 2
to 20 carbon atoms; benzyl; or pyridyl;

30

R^{13} is hydrogen; chlorine; bromine or
alkyl containing 1 to 18 carbon atoms; and

R^{14} and R^{15} are individually aryl
containing 6 to 20 carbon atoms, aralkenyl
containing 6 to 20 carbon atoms; alkyl
containing 1 to 18 carbon atoms; or R^{14}
and R^{15} together represent the carbon
atoms necessary to complete a 7- or

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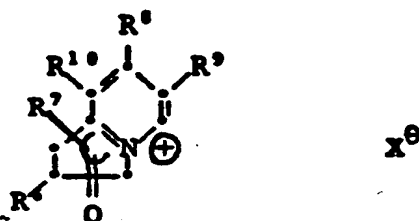
-123-

8-member cyclic structure; and optionally

2) reacting the resulting product from (1)

with a color-forming compound preferably in the
 presence of an oxidant that catalyzes the formation
 of said dye.

3. A method according to Claim 1
 characterized in that said dye compound has the formula:



wherein

X^{\ominus} is an anion;

R^6 and R^7 are individually alkyl
 containing 1 to 18 carbon atoms; aryl
 containing 6 to 20 carbon atoms; or
 polystyryl having appended indolizine or
 indolizinium groups or combinations thereof;

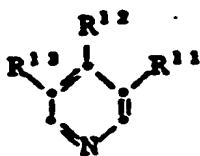
R^8 is a monovalent group which, with
 the indolizinium nucleus, completes an
 organic chromophore;

R^9 is hydrogen; alkyl containing 1 to
 18 carbon atoms; cyano; acyl containing 2
 to 20 carbon atoms; carboalkoxy containing
 2 to 18 carbon atoms; aminocarbonyl
 containing 1 to 18 carbon atoms; acyloxy
 containing 2 to 18 carbon atoms; bromine;
 or chlorine; and

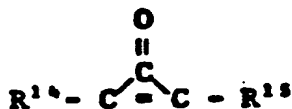
R^{10} is hydrogen; chlorine; bromine; or,

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alkyl containing 1 to 18 carbon atoms;
 which dye compound is prepared by
 1) reacting (A) a pyridine compound having the
 formula:



10 with (B) a cyclopropenone compound represented
 by the formula:



wherein:

R^{11} is hydrogen; alkyl containing 1 to 18
 carbon atoms; cyano; acyl containing 2 to 20
 carbon atoms; carboalkoxy containing 2 to 18
 carbon atoms; aminocarbonyl containing 1 to 18
 carbon atoms; acyloxy containing 2 to 18 carbon
 atoms; bromine or chlorine;

25 R^{12} is hydrogen; alkyl containing 1 to 18
 carbon atoms; cyano; acyl containing 2 to 20
 carbon atoms; benzyl; or pyridyl;

R^{13} is hydrogen; chlorine; bromine or alkyl
 containing 1 to 18 carbon atoms; and

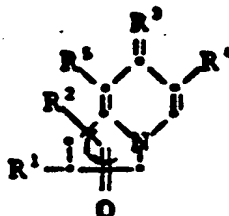
30 R^{14} and R^{15} are individually aryl contain-
 ing 6 to 20 carbon atoms; aralkenyl containing 6
 to 20 carbon atoms; alkyl containing 1 to 18
 carbon atoms; or R^{14} and R^{15} together
 represent the carbon atoms necessary to complete
 a 7- or 8-member cyclic structure; and optionally

35 2) reacting the resulting product from (1) with a
 color-forming compound preferably in the presence of an
 oxidant that catalyzes the formation of said dye;

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the anion X^{\ominus} being provided by the oxidant or color-forming compound (if used) or otherwise.

4. A dye compound having the formula:



5 wherein

R^1 and R^2 are individually alkyl containing 1 to 18 carbon atoms; aryl containing 6 to 20 carbon atoms; or polystyryl having appended indolizine or indolizinium groups or combinations thereof;

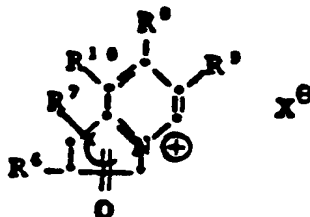
R^3 is a divalent group which, with the indolizinone nucleus, completes an organic chromophore;

R^4 is hydrogen; alkyl containing 1 to 18 carbon atoms; cyano; acyl containing 2 to 20 carbon atoms; carboalkoxy containing 2 to 18 carbon atoms; aminocarbonyl containing 1 to 18 carbon atoms; acyloxy containing 2 to 18 carbon atoms; bromine or chlorine; and

R^5 is hydrogen; chlorine; bromine or alkyl containing 1 to 18 carbon atoms.

5. A dye compound having the formula:

(II)



wherein

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X^{\ominus} is an anion;

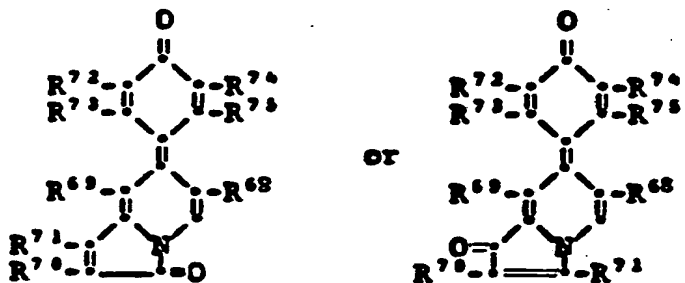
R^6 and R^7 are individually alkyl containing 1 to 18 carbon atoms; aryl containing 6 to 20 carbon atoms; or polystyryl having appended indolizine or indolizinium groups or combinations thereof;

R^8 is a monovalent group which, with the indolizinium nucleus, completes an organic chromophore;

R^9 is hydrogen; alkyl containing 1 to 18 carbon atoms; cyano, acyl containing 2 to 20 carbon atoms; carboalkoxy containing 2 to 18 carbon atoms; aminocarbonyl containing 1 to 18 carbon atoms; acyloxy containing 2 to 18 carbon atoms; bromine or chlorine; and

R^{10} is hydrogen; chlorine; bromine; or alkyl containing 1 to 18 carbon atoms.

6. A dye compound having the formula:



wherein:

R^{68} is hydrogen; alkyl containing 1 to 18 carbon atoms; cyano; acyl containing 2 to 20 carbon atoms; carboalkoxy containing 2 to 18 carbon atoms; aminocarbonyl containing 1 to 18 carbon atoms; acyloxy containing 2 to 18 carbon atoms; bromine; or chlorine;

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R⁶⁹ is hydrogen; chlorine; bromine; or alkyl containing 1 to 18 carbon atoms;

R⁷⁰ and R⁷¹ are individually alkyl containing 1 to 18, preferably 1 to 10 carbon atoms; or aryl containing 6 to 20 carbon atoms;

R⁷² and R⁷³ are individually hydrogen; alkyl containing 1 to 22 carbon atoms, aryl containing 6 to 20 carbon atoms; amino; carboxamido; sulfonamido; sulfamyl; carbamyl; halogen; alkoxy containing 1 to 18 carbon atoms; or R⁷² and R⁷³ taken together represent the atoms necessary to complete a benzo group; and

R⁷⁴ and R⁷⁵ are individually hydrogen; hydroxy; alkyl containing 1 to 22 carbon atoms; aryl containing 6 to 20 carbon atoms; amino; carboxamido; sulfonamido; sulfamyl; carbamyl; halogen; or alkoxy containing 1 to 18 carbon atoms.



European Patent
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EUROPEAN SEARCH REPORT

0068876

Application number

EP 82303381.6

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	No documents have been disclosed		C 09 B 57/00 C 07 D 471/04// G 03 C 1/72 G 03 C 5/16
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 09 B C 07 D 471/00 G 03 C
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons
X	The present search report has been drawn up for all claims		&: member of the same patent family, corresponding document
Place of search VIENNA		Date of completion of the search 06-10-1982	Examiner HAUSWIRTH